

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-119423

(43)Date of publication of application : 12.05.1998

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(51)Int.Cl.

B41M 5/00

B32B 27/00

D21H 27/00

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(21)Application number : 08-283635

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(22)Date of filing : 25.10.1996

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## (54) INK JET RECORDING PAPER

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain an air gap structure, having high ink absorbing property by employing necessary minimum fine solid particles and hydrophilic binder by a method wherein an air gap layer is formed of the soft aggregation or the hydrophilic binder and inorganic fine particles while the hydrophilic binder is crosslinked by hardener.

**SOLUTION:** An air gap structure is formed in a skin film by forming a soft aggregation by a method wherein primary ultrafine particles under a dispersed condition in water solution containing a hydrophilic binder preferably are passed through mutually aggregated condition in a comparatively limited condition of the contacting point thereof. When the primary ultrafine particles are formed in a water solution having a water-soluble binder capable of effecting weak combination between the surface of the primary grains, the amount of air gaps is comparatively easily controlled and formed in a stable, larger amount of air gaps, compared with the amount of fine particles used in this procedure, can be obtained and, further, a film having a high property of luster can be obtained. In this case, the film is hardened by a hardener to obtain a film, having a high void volume without deteriorating the brittleness of the film.

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## LEGAL STATUS

[Date of request for examination] 03.03.2000

[Date of sending the examiner's decision of rejection] 04.12.2001

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3321700

[Date of registration] 28.06.2002

[Number of appeal against examiner's decision of 2001-23528 rejection]

[Date of requesting appeal against examiner's decision of rejection] 28.12.2001

[Date of extinction of right]

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**CLAIMS**

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[Claim(s)]

[Claim 1] The ink jet record form characterized by having the opening layer in which this opening layer was formed of the flocculation of a hydrophilic binder and a non-subtlety particle on the base material in the ink jet record form which has at least one-layer opening layer, and constructing the bridge over this hydrophilic binder with the hardening agent.

[Claim 2] The ink jet record form according to claim 1 characterized by being at least one sort of compounds with which said hydrophilic binder is chosen from polyvinyl alcohol and/or cation conversion polyvinyl alcohol.

[Claim 3] The ink jet record form according to claim 2 characterized by the average degree of polymerization of at least one sort of compounds chosen from said polyvinyl alcohol and/or cation conversion polyvinyl alcohol being 1000 or more.

[Claim 4] The ink jet record form according to claim 1, 2, or 3 with which the non-subtlety particle which said opening layer contains is characterized by being the silica whose mean particle diameter is 5-50nm.

[Claim 5] An ink jet record form given in any 1 term of claims 1-4 characterized by said hardening agents being at least one sort of hardening agents chosen from a way acid or its salt, and/or a poly epoxy system compound.

[Claim 6] An ink jet record form given in any 1 term of claims 1-5 characterized by for said opening layer having at least two hydroxyl groups in a molecule, and molecular weight containing 300 or less polyols.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ink jet record form which has improved the brittleness of a coat and attained altitude spare time capacity in the ink jet record form with which especially an ink absorption layer consists of an opening layer which has high ink absorptivity about the ink jet record form which records using water color ink.

[0002]

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] As an ink jet record form used by this ink jet recording method, also when a printing dot laps [ that a color tone is brightly skillful and absorption of ink ] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [ the concentration of a printing dot is high, and ] beyond the need, and it is required that the circumference should be smooth and should not fade etc.

[0004] Since it becomes nonuniformity, and the color of each other in the border area of a color which a drop causes a HAJIKI phenomenon on an ink jet record form, and is different spreads and it is easy to reduce image quality greatly in case the liquid ink drop of two or more colors laps and is recorded, when especially ink rate of absorption is slow, it is required to give ink absorptivity high as an ink jet record form.

[0005] In order to solve these problems, very many techniques are proposed from the former.

[0006] As the pigment in the clad layer indicated by the ink jet record form which carried out humidity of the coating for surface treatment to the low size stencil indicated by JP,52-53012,A, the ink jet record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and JP,56-157,A The ink jet record form containing non-colloid silica powder, the ink jet record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The ink jet record form which has two hole distribution peaks indicated by JP,58-110287,A, The ink jet record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The ink jet record form which has the infinite form crack indicated by JP,59-68292,A, 59-123696, 60-18383, etc., The ink jet record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, 62-149475, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The ink jet record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-278324,A, 6-92011, 6-183134, 7-137431, The ink jet record form containing particle silicas, such as a colloid silica indicated by 7-276789 etc., And JP,2-276671,A, 3-67684, 3-215082, Many ink jet record forms containing the hydrated alumina particle indicated by 3-251488, 4-67986, 4-263983, 5-16517, etc. are known.

[0007] Generally various kinds of above-mentioned approaches form an opening into a coat, ink is not made to absorb there, and a coat is hardly swollen at the time of ink absorption. For this reason, in case the coat by opening formation receives ink, the amount of openings will be theoretically restricted to below the thickness of a coat.

[0008] For example, in the coat whose desiccation thickness is 40 micrometers, if solid content assumes the coat which is 22 micrometers temporarily as uniform volume, the amount of openings will not have only  $\approx 18\text{ml/m}^2$  per two (40-22) 1m of ink jet record forms, and although based also on a recording method, the case where ink absorption capacity may be insufficient near the amount of the maximum ink will produce it.

[0009] When ink absorption capacity runs short, liquid ink is full of a recording paper front face, and it becomes impossible to obtain a clear image.

[0010] In the coat which has opening structure, in order to attain high void volume, it is most effective to increase spreading thickness, but there is not only disadvantage manufacture top cost increases in this case, but since solid content also increases together, curl and brittleness (film adhesive property [ especially as opposed to the crack or base material under damp ]) of a coat tend to fall greatly.

[0011] For this reason, as many openings as possible are formed using solid content, such as a binder of the minimal dose, and, as for the whole desiccation thickness, decreasing as much as possible is desirable.

[0012] Although the direct approach of raising the void volume to solid content, such as a binder, is making the rate of a non-subtlety particle to a hydrophilic binder increase and it is not using solid content unnecessary otherwise as much as possible, there is a trouble that the brittleness of a coat deteriorates extremely in this case.

[0013] If the brittleness of a coat deteriorates, coat peeling will arise at the time of the time of the handling of an ink jet record form, feeding in an ink jet printer, or conveyance, or a crack will arise, and the serious fault that an image spreads in accordance with this crack will be produced.

[0014] On the other hand, many ink jet record forms of the type which absorbs ink and is held in a swelling operation of the binder of an ink absorption layer are also known, without preparing an opening into a coat.

[0015] For example, many the recording papers, films, etc. which applied hydrophilic binders, such as gelatin, casein, starch, an alginic acid, polyvinyl alcohol, various kinds of conversion polyvinyl alcohol, a polyvinyl pyrrolidone, polyethylene oxide, polypropylene oxide, a carboxymethyl cellulose, HIDOROKI ethyl cellulose, a dextran, and a pullulan, on the base material as binders are known from the former.

[0016] In order that a clear image with high glossiness and optical density may be obtained and these ink jet record forms may receive liquid ink in the swelling operation over the liquid ink of the binder of a coat Although there is an advantage which can hold a high ink absorption capacity intrinsically, ink rate of absorption is inferior compared with the ink jet record form which has opening structure, and has the fault from which the rough deposit by crawling of liquid ink drops tends to arise in the part to which printing of the amount of high ink was carried out especially.

[0017]

[Problem(s) to be Solved by the Invention] The technical problem which this invention is made in view of the above-mentioned actual condition, and this invention tends to solve is to offer the ink jet record form which has the opening structure of high ink absorptivity by the solid-state particle of the need minimum, and the activity of a hydrophilic binder.

[0018]

[Means for Solving the Problem] The above-mentioned object of this invention is attained by the following configurations.

[0019] 1. Ink jet record form characterized by having opening layer in which this opening layer was formed of flocculation of hydrophilic binder and non-subtlety particle on base material in ink jet record form which has at least one-layer opening layer, and constructing bridge over this hydrophilic binder with hardening agent.

[0020] 2. Ink jet record form given in said 1 characterized by being at least one sort of compounds with which said hydrophilic binder is chosen from polyvinyl alcohol and/or cation conversion

polyvinyl alcohol.

[0021] 3. Ink jet record form given in said 2 characterized by average degree of polymerization of at least one sort of compounds chosen from said polyvinyl alcohol and/or cation conversion polyvinyl alcohol being 1000 or more.

[0022] 4. Said 1 and 2 to which non-subtlety particle which said opening layer contains is characterized by being silica whose mean particle diameter is 5–50nm, or ink jet record form given in 3.

[0023] 5. Ink jet record form given in said any 1 term of 1–4 characterized by said hardening agents being at least one sort of hardening agents chosen from way acid or its salt, and/or poly epoxy system compound.

[0024] 6. Ink jet record form given in said any 1 term of 1–5 characterized by for said opening layer having at least two hydroxyl groups in molecule, and molecular weight containing 300 or less polyols.

[0025] Hereafter, this invention is explained to a detail.

[0026] The opening layer which the ink jet record form of this invention has is formed of the binder of a hydrophilic property, and the flocculation of a non-subtlety particle.

[0027] The uniform coating liquid which various the approaches of forming an opening into a coat are learned, for example, contains the polymer beyond \*\*2 sort is conventionally applied on a base material. How to make carry out phase separation of these polymers mutually in a desiccation process, and form an opening, \*\* Apply the coating liquid containing a solid-state particle and a hydrophilic property, or a hydrophobic binder on a base material. How to immerse in the liquid containing water or a suitable organic solvent in an ink jet record form, make dissolve a solid-state particle, and create an opening after desiccation, \*\* After applying the coating liquid containing the compound which has the property which foams at the time of coat formation, The approach of making this compound foam in a desiccation process, and forming an opening into a coat and the coating liquid containing \*\* porosity solid-state particle and a hydrophilic binder are applied on a base material. How to form an opening between the inside of a porosity particle, or a particle, \*\* Or apply the coating liquid containing a particle oil droplet and a hydrophilic binder on a base material. the solid-state particle which has the volume more than equivalent weight (preferably 1.0 or more times) in general to a hydrophilic binder — and — between solid-state particles The approach \*\* mean particle diameter used for the approach and this invention which create an opening carries out flocculation of inorganic solid-state particle about 0.1 micrometers or less at the time of coating liquid preparation or coat formation, forms a secondary particle or the three-dimensional structure, and creates an opening etc. is learned.

[0028] In the ink jet record form of this invention, the opening formation approach by the approach of forming the flocculation of \*\* is used also in having described above from viewpoints, such as high voidage to high glossiness and desiccation thickness, and stability under preservation of opening structure.

[0029] As for the approach of forming the flocculation used by this invention and forming opening structure into a coat, the primary ultrafine particle in a distributed condition is formed into the water solution which contains a hydrophilic binder preferably via the condition that a point of contact condenses each other in the condition of having been restricted comparatively.

[0030] that such flocculation structure is linear or the condition that what formed floc in the shape of branching was distributed in the water solution — or the condition of such flocs condensing each other further and taking the three-dimension network structure in a water solution is included.

[0031] Even if it is which case, detailed opening structure can be formed into the formed coat by carrying out spreading desiccation of this water solution on a base material.

[0032] Thus, in general, from the magnitude of a primary particle, the magnitude of the detailed opening in the obtained coat is about several times those magnitude of this, and has the description which is the opening of detailed magnitude.

[0033] It is formed in the water solution which has the approach of being hard to condense a primary particle to each other, carrying out ultralow-volume addition of the hydrophilic polymer which accelerates condensation of a particle in the water solution containing the hydrophilic binder

which can exist in stability as an approach of forming such flocculation structure, for example, and forming condensation slightly, or the water-soluble binder which can perform a primary particle front face and weak coupling.

[0034] It is desirable from that the latter approach tends to form the amount of an opening in stability especially in this invention that it is comparatively easy to control, that more amounts of openings are obtained as compared with the amount of the particle to be used, and a coat with the still higher glossiness of a coat being obtained.

[0035] When forming an opening by the latter approach, it is desirable from glossiness with higher using a 0.003–0.05-micrometer primary particle in general as a particle size of a primary particle being acquired. Especially a desirable primary particle is a 0.004 micrometers – 0.02 micrometers thing.

[0036] As a non-subtlety particle of this invention, various smectite clay (for example, clay indicated by JP,7-81210,A, 6-184998, etc.), such as silicate, such as a silica, a magnesium silicate, and a calcium silicate, an aluminum hydroxide, zinc hydroxide, and synthetic hectorite, etc. is mentioned, for example.

[0037] Moreover, as a hydrophilic binder of this invention, various well-known hydrophilic binders are used conventionally. For example, gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol, or its derivative (about 20,000 or more have desirable average molecular weight), A polyethylene glycol (100,000 or more have a desirable mean molecular weight), a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, A polyalkylene oxide system copolymerization nature polymer given in locust bean gum, an alginic acid, gum arabic, a pullulan, JP,7-195826,A, and 7-9757, Polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to a water-soluble polyvinyl butyral or JP,62-245260,A. These hydrophilic binders may be used independently and may use two or more sorts together.

[0038] Especially a desirable hydrophilic binder is polyvinyl alcohol or cation conversion polyvinyl alcohol.

[0039] The polyvinyl alcohol preferably used by this invention has desirable average degree of polymerization from the brittleness of the coat from which the thing of 300–4000 is preferably used, and 1000 or more things are obtained especially for average molecular weight being good. Moreover, whenever [ saponification / of polyvinyl alcohol ] has 70 – 100% of desirable thing, and 80 – 100% of especially its thing is desirable. Moreover, cation denaturation polyvinyl alcohol is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0040] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU-(2-acrylamide -2, 2-dimethyl ethyl) ammoniumchloride, TORIMECHIRU-(3-acrylamide -3, 3-dimethyl propyl) ammoniumchloride, N-vinyl imidazole, N-vinyl-2-methylimidazole, N-(3-dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU-(– methacrylamide propyl) ammoniumchloride, N-(1 and 1-dimethyl-3-dimethylaminopropyl) acrylamide, etc. are mentioned.

[0041] the ratio of the cation denaturation radical content monomer of cation denaturation polyvinyl alcohol — vinyl acetate — receiving — 0.1–10-mol % — it is 0.2–5-mol % preferably.

[0042] the polymerization degree of cation denaturation polyvinyl alcohol — usually — 500–4000 – 1000–4000 are preferably desirable.

[0043] whenever [ moreover, / saponification / of cation conversion polyvinyl alcohol ] — usually – 60–100-mol % — it is 70–99-mol % preferably.

[0044] It is the case where especially a desirable thing uses a particle silica as a primary particle by this invention, and polyvinyl alcohol or denaturation polyvinyl alcohol is used as a hydrophilic binder. In this case, hydrogen bond with weak silanol group of a particle silica front face and hydroxyl group of vinyl alcohol is performed, and a flocculation object is formed.

[0045] Especially as a primary particle silica, a thing 0.02 micrometers or less has especially desirable mean particle diameter, and what is 0.015–0.006nm is the most desirable. Moreover, as a

secondary particle which these connected, it is desirable to make it preferably set to about 0.03–0.1 micrometers 0.02–0.2 micrometers.

[0046] The particle silica by which such a particle silica was compounded by the synthetic approach usually called a gaseous-phase method is used preferably.

[0047] In this invention, a hydrophilic binder especially desirable although flocculation structure is formed is polyvinyl alcohol.

[0048] In a weight ratio, the ratios of said hydrophilic binder and said inorganic solid-state particle are 1:15–1:1 in general, and the range of them is 1:10–1:2 preferably.

[0049] The example of the approach is explained below about the case where the coat which contains a flocculation object using polyvinyl alcohol and a particle silica is formed.

[0050] In the polyvinyl alcohol water solution (in general 3 – 15%) which maintained pH at 6–8, and the temperature of about 40 degrees C, it adds gradually, strong-agitating silica particle dispersion liquid (in general 5 – 15%), and an ultrasonic disperser, a high-speed homogenizer, etc. distribute after addition termination. In this case, it is convenient to use the organic solvent of water miscibilities, such as various kinds of surface active agents, a methanol, an acetone, and ethyl acetate, if needed, when preparing uniform coating liquid.

[0051] Subsequently, after adding various kinds of additives, it adjusts to viscosity required for spreading, and the coat which has the above-mentioned opening by applying and drying by the well-known approach on a base material is obtained.

[0052] The ink jet record form of this invention needs to carry out the dura mater of said hydrophilic binder with the hardening agent, in order to obtain high voidage, without degrading the brittleness of a coat.

[0053] Generally, a hardening agent is the compound which promotes the reaction of different radicals which said hydrophilic binder, the compound which has the radical which can react, or a hydrophilic binder has, according to the class of hydrophilic binder, is chosen suitably and used.

[0054] as the example of a hardening agent — for example, an epoxy system hardening agent (diglycidyl ethyl ether —) Ethylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, A 1, 6-diglycidyl cyclohexane, N, and N-diglycidyl 4-glycidyoxy aniline, Sorbitol polyglycidyl ether, glycerol polyglycidyl ether, etc., An aldehyde system hardening agent, an activity halogens (formaldehyde, glyoxal, etc.) system hardening agent (2, 4-dichloro-4-hydroxy – 1, 3, 5-s-triazine, etc.), An activity vinyl system compound, way acids (1, 3, 5-tris acryloyl-hexahydro-s-triazine, bisvinyl-sulfonyl methylether, etc.) and the salt of those, way sand, aluminum alum, etc. are mentioned.

[0055] When using at least one sort of compounds especially chosen from polyvinyl alcohol and/or cation conversion polyvinyl alcohol as a desirable hydrophilic binder, it is desirable to use at least one sort of hardening agents chosen from a way acid and its salt, and/or an epoxy system hardening agent.

[0056] The hardening agent chosen from a way acid and its salt is the most desirable.

[0057] By this invention, as a way acid or its salt, the oxygen acid which uses a boron atom as a neutral atom, and its salt are shown, and an alt-way acid, a 2 way acid, a meta-way acid, tetraboric acid, a 5 way acid, 8 way acids, and those salts are specifically contained.

[0058] Although the amount of the above-mentioned hardening agent used changes with the class of hydrophilic binder, the class of hardening agent, the class of non-subtlety particle, the ratios to a hydrophilic binder, etc., it is 5–100mg preferably 1–200mg per hydrophilic binder 1g in general.

[0059] The above-mentioned hardening agent may be added in the coating liquid which forms the layer of others which reach among the coating liquid of the opening stratification, or adjoin an opening layer in case the coating liquid which constitutes an opening layer is applied. Or although the coating liquid which forms said opening layer on the base material which has applied the coating liquid which contains a hardening agent beforehand can be applied, or the overcoat of the hardening agent solution can be carried out for hardening agent the coating liquid of not containing [ which forms an opening layer further ], after spreading desiccation and a hardening agent can be supplied to an opening layer It is desirable to supply a hardening agent to to add a hardening agent and to form an opening layer preferably, into the coating liquid of the layer which adjoins the coating liquid or this which forms an opening layer, from the effectiveness on manufacture and a viewpoint of the cracking crack prevention at the time of formation of an opening layer, and coincidence.



[0060] Especially, the hardening agent is beforehand added in the coating liquid which forms an opening layer in the desirable mode an ultrafine particle silica and polyvinyl alcohol form [ mode ] an opening layer, and if it applies and dries on a base material after carrying out fixed time amount (preferably 10 minutes or more, especially preferably 30 minutes or more) progress, higher voidage can be attained, without worsening the brittleness of a coat.

[0061] The ink jet record form of this invention can obtain the opening layer in which the brittleness of a coat has been improved further, when an opening layer has at least two hydroxyl groups in a molecule further and molecular weight contains 300 or less polyols.

[0062] As such polyols, ethylene glycol, a diethylene glycol, and a mean molecular weight can mention 300 or less polyethylene glycol, a glycerol, butanediol, butane triol, triethanolamine, etc.

[0063] As for the amount of the above-mentioned polyols used, per [ 0.01–2g ] hydrophilic binder 1g are desirable, and it is the range of 0.05–1g more preferably.

[0064] The ink jet record form of this invention has the remarkable effectiveness of this invention especially in the ink jet record approach of as [ whose amount of the maximum ink is two or more 20 ml/m per two 1m of ink jet record forms ].

[0065] The void volume of the ink jet record form of this invention has the desirable thing of the maximum ink capacity printed which it has especially 95% or more 90% or more. Moreover, the desiccation thickness of the ink absorbing layer which constitutes an opening layer is desirable in order that making it 50 micrometers or less in general may not worsen the physical characteristic of coats, such as a crack.

[0066] On the other hand, as for the ratio to the capacity of the whole opening layer of void volume, it is desirable from the physical reinforcement and the brittle viewpoint of a coat to carry out to below 70 capacity % in general.

[0067] The amount of the range of 20 – 30 ml/m<sup>2</sup> is suitable for the ink jet record form of this invention as void volume with which are satisfied of the above-mentioned conditions.

[0068] In the layer of others which are prepared if needed [ an opening layer and if needed ] for this invention, various kinds of additives can be added besides having described above.

[0069] For example, polystyrene, polyacrylic ester, and polymethacrylic acid ester, Polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, Organic latex particles, such as polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin, A liquid paraffin, dioctyl phthalate, tricresyl phosphate, Various surfactants, such as oil droplet particles, such as a silicone oil, an anion, a cation, and Nonion, An ultraviolet ray absorbent given in JP,57-74193,A, 57-87988, and 62-261476, JP,57-74192,A, 57-87989, 60-72785, The fading inhibitor indicated by 61-146591, JP,1-95091,A, 3-13376, etc., JP,59-42993,A, 59-52689, 62-280069, The fluorescent brightener indicated by 61-242871, JP,4-219266,A, etc., Various well-known additives, such as pH regulators, such as a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0070] Into the configuration layer of the arbitration by the side of the ink recording surface of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56-84992,A, a basic latex polymer of JP,57-36692,A, JP,4-15744,B, JP,61-58788,A, and 62-174184, and given in JP,61-47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0071] The above and an opening layer may consist of more than two-layer, and as long as there is a configuration of those opening layers within limits mentioned above in this case, you may differ.

[0072] Although a thing well-known as a record form for ink jets can be conventionally used suitably as a base material of an ink jet record form by this invention, in order to obtain a clear image by higher concentration, it is desirable to use the hydrophobic base material with which liquid ink does not permeate into a base material.

[0073] The thing of a property which bears the radiant heat when the film which consists of ingredients, such as polyester system resin, diacetate system resin, triacetate system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, being mentioned as a transparency base material, for example, and being used as an OHP especially is desirable, and especially polyethylene terephthalate is desirable. As

thickness of such a transparent base material, about 10–200 micrometers is desirable. It is desirable from an adhesive viewpoint of an ink absorbing layer, a back layer, and a base material to prepare a well-known under-coating layer in an ink absorbing layer [ of a transparency base material ] and back layer side.

[0074] Moreover, the so-called White pet which comes to add white pigments to the resin coat paper (the so-called RC paper) which has the polyolefin resin enveloping layer which added white pigments etc. at least to one side of a base paper as a base material used when there is no transparent need, for example, and polyethylene terephthalate is desirable.

[0075] It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the object, such as to enlarge bond strength of the above-mentioned base material and an ink television layer. Furthermore, the record sheet of this invention does not necessarily need to be colorlessness, and may be a colored record sheet.

[0076] In photograph image quality, near and especially since the image of high quality is moreover obtained by low cost, as for a record image, it is desirable to use the paper base material which laminated both sides of a stencil base material with polyethylene in the ink jet record form of this invention. The paper base material laminated with such polyethylene is explained below.

[0077] The stencil used for a paper base material uses wood pulp as the main raw material, and, in addition to wood pulp, paper making is carried out using synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, if needed. Although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used as wood pulp, it is desirable to use more many [ for a staple fiber ] LBKP, NBSP(s), LBSP(s), and NDP(s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.

[0078] The pulp of the above-mentioned pulp which chemical pulp with few impurities (sulfate pulp and sulfite pulp) was used preferably, and performed bleaching processing, and raised the whiteness degree is also useful.

[0079] In a stencil, flexible-ized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and the 4th class ammonium, etc. can be added suitably.

[0080] The freshness of the pulp used for paper making has desirable 200–500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of 24-mesh residue weight % and weight % for 42-mesh \*\* as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it is desirable that it is 20 or less % of the weight.

[0081] The basis weight of a stencil has 30 thru/or desirable 250g, and 50 thru/or especially its 200g are desirable. The thickness of a stencil has 40 thru/or desirable 250 micrometers.

[0082] After a paper-making phase or paper making, calender processing of the stencil can be carried out and it can also give the Takahira slippage. A stencil consistency has 0.7 thru/or common 1.2 g/m<sup>2</sup> (JIS-P -8118). Furthermore, stencil stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P -8143.

[0083] A surface sizing compound may be applied to a stencil front face, and the same sizing compound as the size which can be added among said stencil as a surface sizing compound can be used for it.

[0084] When pH of a stencil is measured by the hot water extraction method specified by JIS-P-8113, although the polyethylene with which that it is 5–9 cover a desirable stencil front face and a desirable rear face is mainly the polyethylene (LDPE) of a low consistency, and/or polyethylene (HDPE) of high density, a part of other LLDPE(s), polypropylene, etc. can be used for it.

[0085] As for especially the polyethylene layer by the side of an ink absorbing layer, what added the titanium oxide of a rutile or an anatase mold in polyethylene as widely performed by the photographic paper for photographs, and improved opacity and a whiteness degree is desirable. A titanium oxide content is 4 – 13 % of the weight preferably three to 20% of the weight in general to polyethylene.

[0086] polyethylene coat paper can also use the object in which a mat side which performs the so-

called mold attachment processing and is acquired with the usual photographic printing paper, and the silky surface were formed, by this invention, in case melting push appearance also of also using as glossy paper is carried out and it coats polyethylene on a stencil front face.

[0087] After preparing an ink absorbing layer and a back layer, the amount of the polyethylene used of the front flesh side of a stencil is damp and range whose 20–40–micrometer and back layer side the polyethylene layer by the side of an ink absorbing layer is 10–30 micrometers in general, although it is chosen so that the curl by highly–humid–izing may be optimized.

[0088] Furthermore, as for the above–mentioned polyethylene coat paper base material, it is desirable to have the following properties.

[0089] A lengthwise direction by the reinforcement specified by :JIS–P –8113 in hauling strength \*\* 2 thru/or 30kg, A lengthwise direction by the convention approach by JIS–P –8116 \*\* tear reinforcement with desirable longitudinal directions being 1 thru/or 20kg : 10 thru/or 200g, On the conditions specified to JIS–P–8119, \*\* compressibility  $\geq 103$  kgf/cm<sup>2</sup>\*\* surface Beck smoothness with 20 thru/or desirable longitudinal direction 200g : 20 seconds or more, Although 500 seconds or more are especially preferably desirable as a glossy surface, especially 90% or more is desirable 85% or more by the approach by \*\* opacity:JIS–P –8138 which may be less than [ this ] in the so–called mold attachment article.

[0090] The approach of applying various kinds of hydrophilic layers prepared suitably if needed [, such as an opening layer, an under–coating layer, etc. of an ink jet record form of this invention, ] on a base material can be suitably chosen from a well–known approach, and can be performed. A desirable approach paints the coating liquid which constitutes each class on a base material, dries and is acquired. In this case, simultaneous spreading which can also apply more than two–layer simultaneously and substitutes all hydrophilic binder layers for one spreading especially is desirable.

[0091] As a spreading method, the extrusion coat method which uses a hopper the roll coating method, a rod bar coating method, the air–knife–coating method, a spray coating method, the curtain method of application, or given in U.S. Pat. No. 2,681,294 is used preferably.

[0092] In case image recording is carried out using the ink jet record form of this invention, the record approach which used water color ink is used.

[0093] The water color ink said by this invention is the following coloring agent and a solvent object, and a record liquid that consists of other additives. Water soluble dye, such as direct dye well–known as a coloring agent at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used.

[0094] As a solvent of water color ink, water and water–soluble, various organic solvents For example, methyl alcohol, isopropyl alcohol, n–butyl alcohol, Alcohols, such as tert–butyl alcohol and isobutyl alcohol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone–alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6–hexane triol, thiodiglycol, hexylene glycol, Polyhydric alcohol, such as a diethylene glycol, a glycerol, and triethanolamine; Ethylene glycol methyl ether, The low–grade alkyl ether of polyhydric alcohol, such as the diethylene–glycol methyl (or ethyl) ether and the triethylene glycol monobutyl ether, is mentioned.

[0095] Also in the water–soluble organic solvent of these many, the low–grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0096] As an additive of other water color ink, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust–proof, etc. are mentioned, for example.

[0097] In order to make good wettability to an ink jet record form, as for water–color–ink liquid, in 20 degrees C, it is desirable to have the surface tension of 30 – 40 dyn/cm within the limits preferably 25 to 50 dyn/cm.

[0098]

[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples. In addition, in an example, “%”, as long as there is no notice especially,

oven-dry-weight % is shown, and an addition shows the amount per two 1m of ink jet record forms respectively.

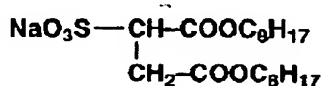
[0099] The front face whose example 1 mean particle diameter is about 0.07 micrometers added 160g of anionic ultrafine particle silica powder in 1000ml of pure water, and distributed with the high-speed homogenizer. next, 5% polyvinyl alcohol water solution (II) (a surfactant -1 is contained 0.3% of the weight) whenever [ saponification / whose ] average degree of polymerization is 90% in 1700 in this silica water dispersion (I) — 1600ml was added gradually. The high-speed homogenizer distributed the obtained liquid and translucent-like coating liquid was obtained.

[0100] Next, the coating liquid obtained as mentioned above was applied to the recording surface side on the paper base material (it is 9% of the weight of anatase mold titanium-dioxide content in the polyethylene layer by the side of 240 micrometers in thickness, and a recording surface.) which covered 170g/stencil both sides of m2 with polyethylene so that humid thickness might be set to 150 micrometers, and it was dried by the 20-40-degree C wind, and the ink jet record form -1 (example of a comparison) was obtained.

[0101]

[Formula 1]

界面活性剤-1



[0102] Next, it is an ink jet record form as well as the ink jet record form -1 except having changed as follows in the ink jet record form -1. -2-9 were created.

[0103] [Ink jet record form -2] It is the same as the ink jet record form -1 except having changed polyvinyl alcohol water-solution (II)1600ml into the mixed liquor of 800ml of 0.3-% of the weight water solutions of polyvinyl alcohol water-solution (II)800ml and a surface active agent -1.

[0104] [Ink jet record form -3] It is the same as the ink jet record form -1 except having changed polyvinyl alcohol water-solution (II)1600ml into the mixed liquor of 1070ml of 0.3-% of the weight water solutions of polyvinyl alcohol water-solution (II)530ml and a surface active agent -1.

[0105] [Ink jet record form -4] It is the same as the ink jet record form -1 except having changed polyvinyl alcohol water-solution (II)1600ml into the mixed liquor of 1200ml of 0.3-% of the weight water solutions of polyvinyl alcohol water-solution (II)400ml and a surface active agent -1.

[0106] [Ink jet record form -5] It is the same as the ink jet record form -1 except having changed polyvinyl alcohol water-solution (II)1600ml into the mixed liquor of 1280ml of 0.3-% of the weight water solutions of polyvinyl alcohol water-solution (II)320ml and a surface active agent -1.

[0107] [Ink jet record form -6] Ink jet record form which applied like the ink jet record form -2, and was obtained after it added 60ml of 2-% of the weight water solutions of tetraboric acid NATORIMU as a hardening agent to the coating liquid used for creating the ink jet record form -2 and the high-speed homogenizer distributed for 30 minutes to it.

[0108] [Ink jet record form -7] Ink jet record form which applied like the ink jet record form -3, and was obtained after it added 50ml of 2-% of the weight water solutions of tetraboric acid NATORIMU as a hardening agent to the coating liquid used for creating the ink jet record form -3 and the high-speed homogenizer distributed for 30 minutes again to it.

[0109] [Ink jet record form -8] Ink jet record form which applied like the ink jet record form -4, and was obtained after it added 60ml of 2-% of the weight water solutions of tetraboric acid NATORIMU as a hardening agent to the coating liquid used for creating the ink jet record form -4 and the high-speed homogenizer distributed for 30 minutes again to it.

[0110] [Ink jet record form -9] Ink jet record form which applied like the ink jet record form -5, and was obtained after it added 70ml of 2-% of the weight water solutions of tetraboric acid NATORIMU as a hardening agent to the coating liquid used for creating the ink jet record form -5 and the high-speed homogenizer distributed for 30 minutes again to it.

[0111] It evaluated about the following items [ form / each / which was obtained / ink jet record ].

[0112] (1) Glossiness : gloss was measured 60 degrees using the deflection glossmeter (VGS-

1001DP) by Nippon Denshoku Industries Co., Ltd.

[0113] (2) The amount of openings : the thin line calculated the amount of the maximum ink which can be identified clearly as an amount of openings, without having printed the thin line pattern of void (un-printing) to the solid field of Y and M, and ink being full of it using the on-demand mold ink jet printer which can control ink discharge quantity.

[0114] (3) ink absorptivity: — although the blot accompanying a crack has crushing of \*\*:shadow section which is not although there is crushing of the image of the shadow section by O:ink overflow which a color picture is printed with the Seiko Epson ink jet printer (MJ-5100C), and there is no crushing of the image of the shadow section by O:ink overflow which evaluated the image quality in a high ink field, and the blot accompanying a crack does not have, either, and there is a blot accompanying a crack — as an image x discriminable in \*\*\*\*: Spread in connection with crushing of an image, the overflow of ink, and a crack, film peeling of the printing section is serious, and it is almost discernment impossible as an image.

[0115] (4) Film formation nature : the film formation nature of a film surface was judged on the following criteria before printing.

[0116]

O : a crack is even if there is nothing and it grinds a front face against a finger strongly with 23 degrees C and 80% of relative humidity. O: in which the film does not separate — although are wound easily at the time of conveyance at x:ink jet printer in which the film does not separate with an ink jet printer at the time of conveyance although it is in the crack condition minute all over [ on which the film does not separate in the usual treatment although the film may separate slightly if there is no crack and it grinds strongly with a finger ] \*\*: and being wound automatically [ after spreading desiccation ] in separating and falling, it separates and falls.

[0117] The obtained result is shown in a table 1.

[0118]

[A table 1]

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-1 (比較例)	7 2 %	11 ml/m <sup>2</sup>	△	○
記録用紙-2 (比較例)	4 2 %	14 ml/m <sup>2</sup>	△	△
記録用紙-3 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-4 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-5 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-6 (本発明)	6 6 %	15 ml/m <sup>2</sup>	○	◎
記録用紙-7 (本発明)	6 2 %	18 ml/m <sup>2</sup>	◎	◎
記録用紙-8 (本発明)	6 0 %	22 ml/m <sup>2</sup>	◎	◎
記録用紙-9 (本発明)	5 6 %	26 ml/m <sup>2</sup>	◎	○

[0119] In the ink jet record form (1-5) which does not use a hardening agent from the result shown in a table 1, When the quantity of the amount of the polyvinyl alcohol to a silica particle is decreased, although the film formation nature as a coat falls and comparatively good film formation nature is obtained for the ratio of the silica to polyvinyl alcohol in 2-4 (ink jet record form - 1 two), the amount of openings is inadequate, in this range, ink absorptivity is insufficient and a good image is not obtained.

[0120] On the other hand, ink jet record form of this invention - It turns out that it has high glossiness and good ink absorptivity, maintaining good film formation nature, even if 6-9 have the outstanding film formation nature and it decreases the amount of polyvinyl alcohol to a silica.

[0121] Ink jet record form created in the example 2 example 1 - It is an ink jet record form like an example 1 except having changed polyvinyl alcohol into 89% of thing average degree of polymerization 700 and whenever [ saponification ] in 1-9. - 11-19 were created.

[0122] The ink jet record form was evaluated like the example 1, and the result shown in a table 2 was obtained.

[0123]

[A table 2]

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-11 (比較例)	48%	10 ml/m <sup>2</sup>	×	△
記録用紙-12 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-13 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-14 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-15 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-16 (本発明)	54%	14 ml/m <sup>2</sup>	△	◎
記録用紙-17 (本発明)	51%	19 ml/m <sup>2</sup>	◎	◎
記録用紙-18 (本発明)	45%	22 ml/m <sup>2</sup>	○	○
記録用紙-19 (本発明)	40%	25 ml/m <sup>2</sup>	○	○

[0124] When the low thing of the average degree of polymerization of polyvinyl alcohol is used from the result shown in a table 2, in not using a hardening agent, it turns out that film formation nature deteriorates also in an ink jet record form (- 1 two) with the comparatively high amount of polyvinyl alcohol, film formation nature is improved by the activity of a hardening agent, and the same effectiveness as an example 1 is acquired although the assessment as an ink jet record form is almost impossible.

[0125] It is an ink jet record form like an example 1 except having changed polyvinyl alcohol into 88% of thing average degree of polymerization 3500 and whenever [ saponification ] in example 3 example 1. - 21-29 were created. The effectiveness same with having been obtained in the place evaluated like the example 1 and the example 1 was checked.

[0126] It sets in the example 4 example 1, and is an ink jet record form. - It is an ink jet record form like an example 1 except having changed the hardening agent into ethylene glycol diglycidyl ether in 6-9 (an addition being the same as that of an example 1). - 36-39 were created and it evaluated like the example 1. A result is shown in a table 3.

[0127]

[A table 3]

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-36 (本発明)	60%	13 ml/m <sup>2</sup>	○	○
記録用紙-37 (本発明)	58%	17 ml/m <sup>2</sup>	○	○
記録用紙-38 (本発明)	52%	21 ml/m <sup>2</sup>	◎	○
記録用紙-39 (本発明)	47%	23 ml/m <sup>2</sup>	◎	○

[0128] The result of a table 3 shows having high film formation nature and ink absorptivity compared with hardening agent un-adding, although film formation nature is a little low compared with a way acid when a hardening agent is changed into an epoxy system compound.

[0129] Ink jet record form created in the example 5 example 1 - Ink jet record form added in 1-9 so that a glycerol might be changed in an opening layer at 0.5 g/m<sup>2</sup> - 41-49 were created and it evaluated like the example 1. The obtained result is shown in a table 4.

[0130]

[A table 4]

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-41 (比較例)	74%	11 ml/m <sup>2</sup>	△	○
記録用紙-42 (比較例)	46%	14 ml/m <sup>2</sup>	△	△
記録用紙-43 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-44 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-45 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-46 (本発明)	72%	14 ml/m <sup>2</sup>	○	◎
記録用紙-47 (本発明)	70%	17 ml/m <sup>2</sup>	◎	◎
記録用紙-48 (本発明)	68%	21 ml/m <sup>2</sup>	◎	◎
記録用紙-49 (本発明)	63%	25 ml/m <sup>2</sup>	◎	◎

[0131] Ink jet record form of the result shown in a table 4 to this invention - As for 46-49, it turns out that film formation nature and glossiness are further improved by addition of a glycerol.

[0132]

[Effect of the Invention] As mentioned above, if the configuration of the ink jet record form of this invention is used, the ink jet record form which has the opening structure of high ink absorptivity and moreover has high glossiness by the solid-state particle of the need minimum and the activity of a hydrophilic binder can be obtained.

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the ink jet record form which has improved the brittleness of a coat and attained altitude spare time capacity in the ink jet record form with which especially an ink absorption layer consists of an opening layer which has high ink absorptivity about the ink jet record form which records using water color ink.

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**PRIOR ART**

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[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-color-izing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread through various fields, such as various printers, facsimile, and a computer terminal, quickly in current.

[0003] As an ink jet record form used by this ink jet recording method, also when a printing dot laps [ that a color tone is brightly skillful and absorption of ink ] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [ the concentration of a printing dot is high, and ] beyond the need, and it is required that the circumference should be smooth and should not fade etc.

[0004] Since it becomes nonuniformity, and the color of each other in the border area of a color which a drop causes a HAJIKI phenomenon on an ink jet record form, and is different spreads and it is easy to reduce image quality greatly in case the liquid ink drop of two or more colors laps and is recorded, when especially ink rate of absorption is slow, it is required to give ink absorptivity high as an ink jet record form.

[0005] In order to solve these problems, very many techniques are proposed from the former.

[0006] As the pigment in the clad layer indicated by the ink jet record form which carried out humidity of the coating for surface treatment to the low size stencil indicated by JP,52-53012,A, the ink jet record form which prepared the coated layer of ink absorptivity in the support surface indicated by JP,55-5830,A, and JP,56-157,A The ink jet record form containing non-colloid silica powder, the ink jet record form which used together the inorganic pigment indicated by JP,57-107878,A and the organic pigment, The ink jet record form which has two hole distribution peaks indicated by JP,58-110287,A, The ink jet record form which consists of a vertical two-layer porous layer indicated by JP,62-111782,A, The ink jet record form which has the infinite form crack indicated by JP,59-68292,A, 59-123696, 60-18383, etc., The ink jet record form which has the impalpable powder layer indicated by JP,61-135786,A, 61-148092, 62-149475, etc., JP,63-252779,A, JP,1-108083,A, 2-136279, The ink jet record form containing the pigment which has the specific physical-properties value indicated by 3-65376, 3-27976, etc., or a particle silica, JP,57-14091,A, 60-219083, 60-210984, 61-20797, 61-188183, JP,5-278324,A, 6-92011, 6-183134, 7-137431, The ink jet record form containing particle silicas, such as a colloid silica indicated by 7-276789 etc., And JP,2-276671,A, 3-67684, 3-215082, Many ink jet record forms containing the hydrated alumina particle indicated by 3-251488, 4-67986, 4-263983, 5-16517, etc. are known.

[0007] Generally various kinds of above-mentioned approaches form an opening into a coat, ink is not made to absorb there, and a coat is hardly swollen at the time of ink absorption. For this reason, in case the coat by opening formation receives ink, the amount of openings will be theoretically restricted to below the thickness of a coat.

[0008] For example, in the coat whose desiccation thickness is 40 micrometers, if solid content assumes the coat which is 22 micrometers temporarily as uniform volume, the amount of openings will not have only =18ml/m<sup>2</sup> per two (40-22) 1m of ink jet record forms, and although based also on

a recording method, the case where ink absorption capacity may be insufficient near the amount of the maximum ink will produce it.

[0009] When ink absorption capacity runs short, liquid ink is full of a recording paper front face, and it becomes impossible to obtain a clear image.

[0010] In the coat which has opening structure, in order to attain high void volume, it is most effective to increase spreading thickness, but there is not only disadvantage manufacture top cost increases in this case, but since solid content also increases together, curl and brittleness (film adhesive property [ especially as opposed to the crack or base material under damp ]) of a coat tend to fall greatly.

[0011] For this reason, as many openings as possible are formed using solid content, such as a binder of the minimal dose, and, as for the whole desiccation thickness, decreasing as much as possible is desirable.

[0012] Although the direct approach of raising the void volume to solid content, such as a binder, is making the rate of a non-subtlety particle to a hydrophilic binder increase and it is not using solid content unnecessary otherwise as much as possible, there is a trouble that the brittleness of a coat deteriorates extremely in this case.

[0013] If the brittleness of a coat deteriorates, coat peeling will arise at the time of the time of the handling of an ink jet record form, feeding in an ink jet printer, or conveyance, or a crack will arise, and the serious fault that an image spreads in accordance with this crack will be produced.

[0014] On the other hand, many ink jet record forms of the type which absorbs ink and is held in a swelling operation of the binder of an ink absorption layer are also known, without preparing an opening into a coat.

[0015] For example, many the recording papers, films, etc. which applied hydrophilic binders, such as gelatin, casein, starch, an alginic acid, polyvinyl alcohol, various kinds of conversion polyvinyl alcohol, a polyvinyl pyrrolidone, polyethylene oxide, polypropylene oxide, a carboxymethyl cellulose, HIDOROKI ethyl cellulose, a dextran, and a pullulan, on the base material as binders are known from the former.

[0016] In order that a clear image with high glossiness and optical density may be obtained and these ink jet record forms may receive liquid ink in the swelling operation over the liquid ink of the binder of a coat Although there is an advantage which can hold a high ink absorption capacity intrinsically, ink rate of absorption is inferior compared with the ink jet record form which has opening structure, and has the fault from which the rough deposit by crawling of liquid ink drops tends to arise in the part to which printing of the amount of high ink was carried out especially.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] As mentioned above, if the configuration of the ink jet record form of this invention is used, the ink jet record form which has the opening structure of high ink absorptivity and moreover has high glossiness by the solid-state particle of the need minimum and the activity of a hydrophilic binder can be obtained.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] The technical problem which this invention is made in view of the above-mentioned actual condition, and this invention tends to solve is to offer the ink jet record form which has the opening structure of high ink absorptivity by the solid-state particle of the need minimum, and the activity of a hydrophilic binder.

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**MEANS**

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[Means for Solving the Problem] The above-mentioned object of this invention is attained by the following configurations.

[0019] 1. Ink jet record form characterized by having opening layer in which this opening layer was formed of flocculation of hydrophilic binder and non-subtlety particle on base material in ink jet record form which has at least one-layer opening layer, and constructing bridge over this hydrophilic binder with hardening agent.

[0020] 2. Ink jet record form given in said 1 characterized by being at least one sort of compounds with which said hydrophilic binder is chosen from polyvinyl alcohol and/or cation conversion polyvinyl alcohol.

[0021] 3. Ink jet record form given in said 2 characterized by average degree of polymerization of at least one sort of compounds chosen from said polyvinyl alcohol and/or cation conversion polyvinyl alcohol being 1000 or more.

[0022] 4. Said 1 and 2 to which non-subtlety particle which said opening layer contains is characterized by being silica whose mean particle diameter is 5-50nm, or ink jet record form given in 3.

[0023] 5. Ink jet record form given in said any 1 term of 1-4 characterized by said hardening agents being at least one sort of hardening agents chosen from way acid or its salt, and/or poly epoxy system compound.

[0024] 6. Ink jet record form given in said any 1 term of 1-5 characterized by for said opening layer having at least two hydroxyl groups in molecule, and molecular weight containing 300 or less polyols.

[0025] Hereafter, this invention is explained to a detail.

[0026] The opening layer which the ink jet record form of this invention has is formed of the binder of a hydrophilic property, and the flocculation of a non-subtlety particle.

[0027] The uniform coating liquid which various the approaches of forming an opening into a coat are learned, for example, contains the polymer beyond \*\*2 sort is conventionally applied on a base material. How to make carry out phase separation of these polymers mutually in a desiccation process, and form an opening, \*\* Apply the coating liquid containing a solid-state particle and a hydrophilic property, or a hydrophobic binder on a base material. How to immerse in the liquid containing water or a suitable organic solvent in an ink jet record form, make dissolve a solid-state particle, and create an opening after desiccation, \*\* After applying the coating liquid containing the compound which has the property which foams at the time of coat formation, The approach of making this compound foam in a desiccation process, and forming an opening into a coat and the coating liquid containing \*\* porosity solid-state particle and a hydrophilic binder are applied on a base material. How to form an opening between the inside of a porosity particle, or a particle, \*\* Or apply the coating liquid containing a particle oil droplet and a hydrophilic binder on a base material. the solid-state particle which has the volume more than equivalent weight (preferably 1.0 or more times) in general to a hydrophilic binder — and — between solid-state particles The approach \*\* mean particle diameter used for the approach and this invention which create an opening carries out flocculation of inorganic solid-state particle about 0.1 micrometers or less at the time of coating liquid preparation or coat formation, forms a secondary particle or the three-dimensional

structure, and creates an opening etc. is learned.

[0028] In the ink jet record form of this invention, the opening formation approach by the approach of forming the flocculation of \*\* is used also in having described above from viewpoints, such as high voidage to high glossiness and desiccation thickness, and stability under preservation of opening structure.

[0029] As for the approach of forming the flocculation used by this invention and forming opening structure into a coat, the primary ultrafine particle in a distributed condition is formed into the water solution which contains a hydrophilic binder preferably via the condition that a point of contact condenses each other in the condition of having been restricted comparatively.

[0030] that such flocculation structure is linear or the condition that what formed floc in the shape of branching was distributed in the water solution — or the condition of such flocs condensing each other further and taking the three-dimension network structure in a water solution is included.

[0031] Even if it is which case, detailed opening structure can be formed into the formed coat by carrying out spreading desiccation of this water solution on a base material.

[0032] Thus, in general, from the magnitude of a primary particle, the magnitude of the detailed opening in the obtained coat is about several times those magnitude of this, and has the description which is the opening of detailed magnitude.

[0033] It is formed in the water solution which has the approach of being hard to condense a primary particle to each other, carrying out ultralow-volume addition of the hydrophilic polymer which accelerates condensation of a particle in the water solution containing the hydrophilic binder which can exist in stability as an approach of forming such flocculation structure, for example, and forming condensation slightly, or the water-soluble binder which can perform a primary particle front face and weak coupling.

[0034] It is desirable from that the latter approach tends to form the amount of an opening in stability especially in this invention that it is comparatively easy to control, that more amounts of openings are obtained as compared with the amount of the particle to be used, and a coat with the still higher glossiness of a coat being obtained.

[0035] When forming an opening by the latter approach, it is desirable from glossiness with higher using a 0.003–0.05-micrometer primary particle in general as a particle size of a primary particle being acquired. Especially a desirable primary particle is a 0.004 micrometers – 0.02 micrometers thing.

[0036] As a non-subtlety particle of this invention, various smectite clay (for example, clay indicated by JP,7-81210,A, 6-184998, etc.), such as silicate, such as a silica, a magnesium silicate, and a calcium silicate, an aluminum hydroxide, zinc hydroxide, and synthetic hectorite, etc. is mentioned, for example.

[0037] Moreover, as a hydrophilic binder of this invention, various well-known hydrophilic binders are used conventionally. For example, gelatin or a gelatin derivative, a polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), A pullulan, polyvinyl alcohol, or its derivative (about 20,000 or more have desirable average molecular weight), A polyethylene glycol (100,000 or more have a desirable mean molecular weight), a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, A polyalkylene oxide system copolymerization nature polymer given in locust bean gum, an alginic acid, gum arabic, a pullulan, JP,7-195826,A, and 7-9757, Polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to a water-soluble polyvinyl butyral or JP,62-245260,A. These hydrophilic binders may be used independently and may use two or more sorts together.

[0038] Especially a desirable hydrophilic binder is polyvinyl alcohol or cation conversion polyvinyl alcohol.

[0039] The polyvinyl alcohol preferably used by this invention has desirable average degree of polymerization from the brittleness of the coat from which the thing of 300–4000 is preferably used, and 1000 or more things are obtained especially for average molecular weight being good. Moreover, whenever [ saponification / of polyvinyl alcohol ] has 70 – 100% of desirable thing, and

80 – 100% of especially its thing is desirable. Moreover, cation denaturation polyvinyl alcohol is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0040] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU-(2-acrylamide -2, 2-dimethyl ethyl) ammoniumchloride, TORIMECHIRU-(3-acrylamide -3, 3-dimethyl propyl) ammoniumchloride, N-vinyl imidazole, N-vinyl-2-methylimidazole, N-(3-dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU-(methacrylamide propyl) ammoniumchloride, N-(1 and 1-dimethyl-3-dimethylaminopropyl) acrylamide, etc. are mentioned.

[0041] the ratio of the cation denaturation radical content monomer of cation denaturation polyvinyl alcohol — vinyl acetate — receiving — 0.1–10-mol % — it is 0.2–5-mol % preferably.

[0042] the polymerization degree of cation denaturation polyvinyl alcohol — usually — 500–4000 — 1000–4000 are preferably desirable.

[0043] whenever [ moreover, / saponification / of cation conversion polyvinyl alcohol ] — usually — 60–100-mol % — it is 70–99-mol % preferably.

[0044] It is the case where especially a desirable thing uses a particle silica as a primary particle by this invention, and polyvinyl alcohol or denaturation polyvinyl alcohol is used as a hydrophilic binder. In this case, hydrogen bond with weak silanol group of a particle silica front face and hydroxyl group of vinyl alcohol is performed, and a flocculation object is formed.

[0045] Especially as a primary particle silica, a thing 0.02 micrometers or less has especially desirable mean particle diameter, and what is 0.015–0.006nm is the most desirable. Moreover, as a secondary particle which these connected, it is desirable to make it preferably set to about 0.03–0.1 micrometers 0.02–0.2 micrometers.

[0046] The particle silica by which such a particle silica was compounded by the synthetic approach usually called a gaseous-phase method is used preferably.

[0047] In this invention, a hydrophilic binder especially desirable although flocculation structure is formed is polyvinyl alcohol.

[0048] In a weight ratio, the ratios of said hydrophilic binder and said inorganic solid-state particle are 1:15–1:1 in general, and the range of them is 1:10–1:2 preferably.

[0049] The example of the approach is explained below about the case where the coat which contains a flocculation object using polyvinyl alcohol and a particle silica is formed.

[0050] In the polyvinyl alcohol water solution (in general 3 – 15%) which maintained pH at 6–8, and the temperature of about 40 degrees C, it adds gradually, strong-agitating silica particle dispersion liquid (in general 5 – 15%), and an ultrasonic disperser, a high-speed homogenizer, etc. distribute after addition termination. In this case, it is convenient to use the organic solvent of water miscibilities, such as various kinds of surface active agents, a methanol, an acetone, and ethyl acetate, if needed, when preparing uniform coating liquid.

[0051] Subsequently, after adding various kinds of additives, it adjusts to viscosity required for spreading, and the coat which has the above-mentioned opening by applying and drying by the well-known approach on a base material is obtained.

[0052] The ink jet record form of this invention needs to carry out the dura mater of said hydrophilic binder with the hardening agent, in order to obtain high voidage, without degrading the brittleness of a coat.

[0053] Generally, a hardening agent is the compound which promotes the reaction of different radicals which said hydrophilic binder, the compound which has the radical which can react, or a hydrophilic binder has, according to the class of hydrophilic binder, is chosen suitably and used.

[0054] as the example of a hardening agent — for example, an epoxy system hardening agent (diglycidyl ethyl ether —) Ethylene glycol diglycidyl ether, 1,4-butanediol diglycidyl ether, A 1, 6-diglycidyl cyclohexane, N, and N-diglycidyl 4-glycidyloxy aniline, Sorbitol polyglycidyl ether, glycerol polyglycidyl ether, etc., An aldehyde system hardening agent, an activity halogens (formaldehyde, glyoxal, etc.) system hardening agent (2, 4-dichloro-4-hydroxy – 1, 3, 5-s-triazine, etc.), An activity vinyl system compound, way acids (1, 3, 5-tris acryloyl-hexahydro-s-triazine, bisvinyl-sulfonyl methylether, etc.) and the salt of those, way sand, aluminum alum, etc. are mentioned.

[0055] When using at least one sort of compounds especially chosen from polyvinyl alcohol and/or

cation conversion polyvinyl alcohol as a desirable hydrophilic binder, it is desirable to use at least one sort of hardening agents chosen from a way acid and its salt, and/or an epoxy system hardening agent.

[0056] The hardening agent chosen from a way acid and its salt is the most desirable.

[0057] By this invention, as a way acid or its salt, the oxygen acid which uses a boron atom as a neutral atom, and its salt are shown, and an alt way acid, a 2 way acid, a meta-way acid, tetraboric acid, a 5 way acid, 8 way acids, and those salts are specifically contained.

[0058] Although the amount of the above-mentioned hardening agent used changes with the class of hydrophilic binder, the class of hardening agent, the class of non-subtlety particle, the ratios to a hydrophilic binder, etc., it is 5-100mg preferably 1-200mg per hydrophilic binder 1g in general.

[0059] The above-mentioned hardening agent may be added in the coating liquid which forms the layer of others which reach among the coating liquid of the opening stratification, or adjoin an opening layer in case the coating liquid which constitutes an opening layer is applied. Or although the coating liquid which forms said opening layer on the base material which has applied the coating liquid which contains a hardening agent beforehand can be applied, or the overcoat of the hardening agent solution can be carried out for hardening agent the coating liquid of not containing [ which forms an opening layer further ], after spreading desiccation and a hardening agent can be supplied to an opening layer. It is desirable to supply a hardening agent to to add a hardening agent and to form an opening layer preferably, into the coating liquid of the layer which adjoins the coating liquid or this which forms an opening layer, from the effectiveness on manufacture and a viewpoint of the cracking crack prevention at the time of formation of an opening layer, and coincidence.

[0060] Especially, the hardening agent is beforehand added in the coating liquid which forms an opening layer in the desirable mode an ultrafine particle silica and polyvinyl alcohol form [ mode ] an opening layer, and if it applies and dries on a base material after carrying out fixed time amount (preferably 10 minutes or more, especially preferably 30 minutes or more) progress, higher voidage can be attained, without worsening the brittleness of a coat.

[0061] The ink jet record form of this invention can obtain the opening layer in which the brittleness of a coat has been improved further, when an opening layer has at least two hydroxyl groups in a molecule further and molecular weight contains 300 or less polyols.

[0062] As such polyols, ethylene glycol, a diethylene glycol, and a mean molecular weight can mention 300 or less polyethylene glycol, a glycerol, butanediol, butane triol, triethanolamine, etc.

[0063] As for the amount of the above-mentioned polyols used, per [ 0.01-2g ] hydrophilic binder 1g are desirable, and it is the range of 0.05-1g more preferably.

[0064] The ink jet record form of this invention has the remarkable effectiveness of this invention especially in the ink jet record approach of as [ whose amount of the maximum ink is two or more 20 ml/m per two 1m of ink jet record forms ].

[0065] The void volume of the ink jet record form of this invention has the desirable thing of the maximum ink capacity printed which it has especially 95% or more 90% or more. Moreover, the desiccation thickness of the ink absorbing layer which constitutes an opening layer is desirable in order that making it 50 micrometers or less in general may not worsen the physical characteristic of coats, such as a crack.

[0066] On the other hand, as for the ratio to the capacity of the whole opening layer of void volume, it is desirable from the physical reinforcement and the brittle viewpoint of a coat to carry out to below 70 capacity % in general.

[0067] The amount of the range of 20 - 30 ml/m<sup>2</sup> is suitable for the ink jet record form of this invention as void volume with which are satisfied of the above-mentioned conditions.

[0068] In the layer of others which are prepared if needed [ an opening layer and if needed ] for this invention, various kinds of additives can be added besides having described above.

[0069] For example, polystyrene, polyacrylic ester, and polymethacrylic acid ester, Polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, Organic latex particles, such as polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin, A liquid paraffin, dioctyl phthalate, tricresyl phosphate, Various surfactants, such as oil droplet particles, such as a silicone oil, an anion, a cation, and Nonion, An ultraviolet ray absorbent given in JP,57-74193,A, 57-87988, and 62-261476, JP,57-74192,A, 57-87989, 60-72785, The fading inhibitor indicated by 61-146591,



JP,1-95091,A, 3-13376, etc., JP,59-42993,A, 59-52689, 62-280069, The fluorescent brightener indicated by 61-242871, JP,4-219266,A, etc., Various well-known additives, such as pH regulators, such as a sulfuric acid, a phosphoric acid, a citric acid, a sodium hydroxide, a potassium hydroxide, and potassium carbonate, a defoaming agent, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0070] Into the configuration layer of the arbitration by the side of the ink recording surface of this invention, an alkali-metal weak acid salt the poly allylamine of publications, such as the poly cation polyelectrolyte of JP,56-84992,A, a basic latex polymer of JP,57-36692,A, JP,4-15744,B, JP,61-58788,A, and 62-174184, and given in JP,61-47290,A etc. can be used more than a kind as a deck-watertight-luminaire-ized agent of an image.

[0071] The above and an opening layer may consist of more than two-layer, and as long as there is a configuration of those opening layers within limits mentioned above in this case, you may differ.

[0072] Although a thing well-known as a record form for ink jets can be conventionally used suitably as a base material of an ink jet record form by this invention, in order to obtain a clear image by higher concentration, it is desirable to use the hydrophobic base material with which liquid ink does not permeate into a base material.

[0073] The thing of a property which bears the radiant heat when the film which consists of ingredients, such as polyester system resin, diacetate system resin, triacetate system resin, acrylic resin, polycarbonate system resin, polyvinyl chloride system resin, polyimide system resin, cellophane, and celluloid, being mentioned as a transparence base material, for example, and being used as an OHP especially is desirable, and especially polyethylene terephthalate is desirable. As thickness of such a transparent base material, about 10-200 micrometers is desirable. It is desirable from an adhesive viewpoint of an ink absorbing layer, a back layer, and a base material to prepare a well-known under-coating layer in an ink absorbing layer [ of a transparence base material ] and back layer side.

[0074] Moreover, the so-called White pet which comes to add white pigments to the resin coat paper (the so-called RC paper) which has the polyolefin resin enveloping layer which added white pigments etc. at least to one side of a base paper as a base material used when there is no transparent need, for example, and polyethylene terephthalate is desirable.

[0075] It is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of an ink absorbing layer for the object, such as to enlarge bond strength of the above-mentioned base material and an ink television layer. Furthermore, the record sheet of this invention does not necessarily need to be colorlessness, and may be a colored record sheet.

[0076] In photograph image quality, near and especially since the image of high quality is moreover obtained by low cost, as for a record image, it is desirable to use the paper base material which laminated both sides of a stencil base material with polyethylene in the ink jet record form of this invention. The paper base material laminated with such polyethylene is explained below.

[0077] The stencil used for a paper base material uses wood pulp as the main raw material, and, in addition to wood pulp, paper making is carried out using synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, if needed. Although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used as wood pulp, it is desirable to use more many [ for a staple fiber ] LBKP, NBSP(s), LBSP(s), and NDP(s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.

[0078] The pulp of the above-mentioned pulp which chemical pulp with few impurities (sulfate pulp and sulfite pulp) was used preferably, and performed bleaching processing, and raised the whiteness degree is also useful.

[0079] In a stencil, flexible-ized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and the 4th class ammonium, etc. can be added suitably.

[0080] The freshness of the pulp used for paper making has desirable 200-500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of 24-mesh residue weight % and weight % for 42-

mesh \*\* as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it is desirable that it is 20 or less % of the weight.

[0081] The basis weight of a stencil has 30 thru/or desirable 250g, and 50 thru/or especially its 200g are desirable. The thickness of a stencil has 40 thru/or desirable 250 micrometers.

[0082] After a paper-making phase or paper making, calender processing of the stencil can be carried out and it can also give the Takahira slippage. A stencil consistency has 0.7 thru/or common 1.2 g/m<sup>2</sup> (JIS-P -8118). Furthermore, stencil stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P -8143.

[0083] A surface sizing compound may be applied to a stencil front face, and the same sizing compound as the size which can be added among said stencil as a surface sizing compound can be used for it.

[0084] When pH of a stencil is measured by the hot water extraction method specified by JIS-P-8113, although the polyethylene with which that it is 5-9 cover a desirable stencil front face and a desirable rear face is mainly the polyethylene (LDPE) of a low consistency, and/or polyethylene (HDPE) of high density, a part of other LLDPE(s), polypropylene, etc. can be used for it.

[0085] As for especially the polyethylene layer by the side of an ink absorbing layer, what added the titanium oxide of a rutile or an anatase mold in polyethylene as widely performed by the photographic paper for photographs, and improved opacity and a whiteness degree is desirable. A titanium oxide content is 4 - 13 % of the weight preferably three to 20% of the weight in general to polyethylene.

[0086] polyethylene coat paper can also use the object in which a mat side which performs the so-called mold attachment processing and is acquired with the usual photographic printing paper, and the silky surface were formed, by this invention, in case melting push appearance also of also using as glossy paper is carried out and it coats polyethylene on a stencil front face.

[0087] After preparing an ink absorbing layer and a back layer, the amount of the polyethylene used of the front flesh side of a stencil is damp and range whose 20-40-micrometer and back layer side the polyethylene layer by the side of an ink absorbing layer is 10-30 micrometers in general, although it is chosen so that the curl by highly-humid-izing may be optimized.

[0088] Furthermore, as for the above-mentioned polyethylene coat paper base material, it is desirable to have the following properties.

[0089] A lengthwise direction by the reinforcement specified by :JIS-P -8113 in hauling strength \*\* 2 thru/or 30kg, A lengthwise direction by the convention approach by JIS-P -8116 \*\* tear reinforcement with desirable longitudinal directions being 1 thru/or 20kg : 10 thru/or 200g, On the conditions specified to JIS-P-8119, \*\* compressibility  $\geq 103$  kgf/cm<sup>2</sup>\*\* surface Beck smoothness with 20 thru/or desirable longitudinal direction 200g : 20 seconds or more, Although 500 seconds or more are especially preferably desirable as a glossy surface, especially 90% or more is desirable 85% or more by the approach by \*\* opacity:JIS-P -8138 which may be less than [ this ] in the so-called mold attachment article.

[0090] The approach of applying various kinds of hydrophilic layers prepared suitably if needed [, such as an opening layer, an under-coating layer, etc. of an ink jet record form of this invention, ] on a base material can be suitably chosen from a well-known approach, and can be performed. A desirable approach paints the coating liquid which constitutes each class on a base material, dries and is acquired. In this case, simultaneous spreading which can also apply more than two-layer simultaneously and substitutes all hydrophilic binder layers for one spreading especially is desirable.

[0091] As a spreading method, the extrusion coat method which uses a hopper the roll coating method, a rod bar coating method, the air-knife-coating method, a spray coating method, the curtain method of application, or given in U.S. Pat. No. 2,681,294 is used preferably.

[0092] In case image recording is carried out using the ink jet record form of this invention, the record approach which used water color ink is used.

[0093] The water color ink said by this invention is the following coloring agent and a solvent object, and a record liquid that consists of other additives. Water soluble dye, such as direct dye well-known as a coloring agent at an ink jet, acid dye, basic dye, reactive dye, or a food dye, can be used.

[0094] As a solvent of water color ink, water and water-soluble, various organic solvents For example, methyl alcohol, isopropyl alcohol, n-butyl alcohol, Alcohols, such as tert-butyl alcohol and isobutyl alcohol; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone-alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, Polyhydric alcohol, such as a diethylene glycol, a glycerol, and triethanolamine; Ethylene glycol methyl ether, The low-grade alkyl ether of polyhydric alcohol, such as the diethylene-glycol methyl (or ethyl) ether and the triethylene glycol monobutyl ether, is mentioned.

[0095] Also in the water-soluble organic solvent of these many, the low-grade alkyl ether of the polyhydric alcohol of polyhydric alcohol, such as a diethylene glycol, triethanolamine, and a glycerol, and the triethylene glycol monobutyl ether etc. is desirable.

[0096] As an additive of other water color ink, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proofer, etc. are mentioned, for example.

[0097] In order to make good wettability to an ink jet record form, as for water-color-ink liquid, in 20 degrees C, it is desirable to have the surface tension of 30 – 40 dyn/cm within the limits preferably 25 to 50 dyn/cm.

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[Translation done.]

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EXAMPLE

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[Example] Although the example of this invention is given and explained below, this invention is not limited to these examples. In addition, in an example, "%", as long as there is no notice especially, oven-dry-weight % is shown, and an addition shows the amount per two 1m of ink jet record forms respectively.

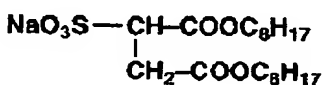
[0099] The front face whose example 1 mean particle diameter is about 0.07 micrometers added 160g of anionic ultrafine particle silica powder in 1000ml of pure water, and distributed with the high-speed homogenizer. next, 5% polyvinyl alcohol water solution (II) (a surfactant -1 is contained 0.3% of the weight) whenever [ saponification / whose ] average degree of polymerization is 90% in 1700 in this silica water dispersion (I) — 1600ml was added gradually. The high-speed homogenizer distributed the obtained liquid and translucent-like coating liquid was obtained.

[0100] Next, the coating liquid obtained as mentioned above was applied to the recording surface side on the paper base material (it is 9% of the weight of anatase mold titanium-dioxide content in the polyethylene layer by the side of 240 micrometers in thickness, and a recording surface.) which covered 170g/stencil both sides of m2 with polyethylene so that humid thickness might be set to 150 micrometers, and it was dried by the 20-40-degree C wind, and the ink jet record form -1 (example of a comparison) was obtained.

[0101]

[Formula 1]

界面活性剤-1



[0102] Next, it is an ink jet record form as well as the ink jet record form -1 except having changed as follows in the ink jet record form -1. - 2-9 were created.

[0103] [Ink jet record form -2] It is the same as the ink jet record form -1 except having changed polyvinyl alcohol water-solution (II)1600ml into the mixed liquor of 800ml of 0.3-% of the weight water solutions of polyvinyl alcohol water-solution (II)800ml and a surface active agent -1.

[0104] [Ink jet record form -3] It is the same as the ink jet record form -1 except having changed polyvinyl alcohol water-solution (II)1600ml into the mixed liquor of 1070ml of 0.3-% of the weight water solutions of polyvinyl alcohol water-solution (II)530ml and a surface active agent -1.

[0105] [Ink jet record form -4] It is the same as the ink jet record form -1 except having changed polyvinyl alcohol water-solution (II)1600ml into the mixed liquor of 1200ml of 0.3-% of the weight water solutions of polyvinyl alcohol water-solution (II)400ml and a surface active agent -1.

[0106] [Ink jet record form -5] It is the same as the ink jet record form -1 except having changed polyvinyl alcohol water-solution (II)1600ml into the mixed liquor of 1280ml of 0.3-% of the weight water solutions of polyvinyl alcohol water-solution (II)320ml and a surface active agent -1.

[0107] [Ink jet record form -6] Ink jet record form which applied like the ink jet record form -2, and was obtained after it added 60ml of 2-% of the weight water solutions of tetraboric acid NATORIMU as a hardening agent to the coating liquid used for creating the ink jet record form -2 and the high-

speed homogenizer distributed for 30 minutes to it.

[0108] [Ink jet record form -7] Ink jet record form which applied like the ink jet record form -3, and was obtained after it added 50ml of 2-% of the weight water solutions of tetraboric acid NATORIMU as a hardening agent to the coating liquid used for creating the ink jet record form -3 and the high-speed homogenizer distributed for 30 minutes again to it.

[0109] [Ink jet record form -8] Ink jet record form which applied like the ink jet record form -4, and was obtained after it added 60ml of 2-% of the weight water solutions of tetraboric acid NATORIMU as a hardening agent to the coating liquid used for creating the ink jet record form -4 and the high-speed homogenizer distributed for 30 minutes again to it.

[0110] [Ink jet record form -9] Ink jet record form which applied like the ink jet record form -5, and was obtained after it added 70ml of 2-% of the weight water solutions of tetraboric acid NATORIMU as a hardening agent to the coating liquid used for creating the ink jet record form -5 and the high-speed homogenizer distributed for 30 minutes again to it.

[0111] It evaluated about the following items [ form / each / which was obtained / ink jet record ].

[0112] (1) Glossiness : gloss was measured 60 degrees using the deflection glossmeter (VGS-1001DP) by Nippon Denshoku Industries Co., Ltd.

[0113] (2) The amount of openings : the thin line calculated the amount of the maximum ink which can be identified clearly as an amount of openings, without having printed the thin line pattern of void (un-printing) to the solid field of Y and M, and ink being full of it using the on-demand mold ink jet printer which can control ink discharge quantity.

[0114] (3) ink absorptivity: — although the blot accompanying a crack has crushing of \*\*:shadow section which is not although there is crushing of the image of the shadow section by O:ink overflow which a color picture is printed with the Seiko Epson ink jet printer (MJ-5100C), and there is no crushing of the image of the shadow section by O:ink overflow which evaluated the image quality in a high ink field, and the blot accompanying a crack does not have, either, and there is a blot accompanying a crack — as an image x discriminable in \*\*\*\*: Spread in connection with crushing of an image, the overflow of ink, and a crack, film peeling of the printing section is serious, and it is almost discernment impossible as an image.

[0115] (4) Film formation nature : the film formation nature of a film surface was judged on the following criteria before printing.

[0116]

O : a crack is even if there is nothing and it grinds a front face against a finger strongly with 23 degrees C and 80% of relative humidity. O: in which the film does not separate — although are wound easily at the time of conveyance at x:ink jet printer in which the film does not separate with an ink jet printer at the time of conveyance although it is in the crack condition minute all over [ on which the film does not separate in the usual treatment although the film may separate slightly if there is no crack and it grinds strongly with a finger ] \*\*: and being wound automatically [ after spreading desiccation ] in separating and falling, it separates and falls.

[0117] The obtained result is shown in a table 1.

[0118]

[A table 1]

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-1 (比較例)	7 2 %	11 ml/m <sup>2</sup>	△	○
記録用紙-2 (比較例)	4 2 %	14 ml/m <sup>2</sup>	△	△
記録用紙-3 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-4 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-5 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-6 (本発明)	6 6 %	15 ml/m <sup>2</sup>	○	◎
記録用紙-7 (本発明)	6 2 %	18 ml/m <sup>2</sup>	◎	◎
記録用紙-8 (本発明)	6 0 %	22 ml/m <sup>2</sup>	◎	◎
記録用紙-9 (本発明)	5 6 %	26 ml/m <sup>2</sup>	◎	○

[0119] In the ink jet record form (1-5) which does not use a hardening agent from the result shown in a table 1, When the quantity of the amount of the polyvinyl alcohol to a silica particle is

decreased, although the film formation nature as a coat falls and comparatively good film formation nature is obtained for the ratio of the silica to polyvinyl alcohol in 2-4 (ink jet record form - 1 two), the amount of openings is inadequate, in this range, ink absorptivity is insufficient and a good image is not obtained.

[0120] On the other hand, ink jet record form of this invention - It turns out that it has high glossiness and good ink absorptivity, maintaining good film formation nature, even if 6-9 have the outstanding film formation nature and it decreases the amount of polyvinyl alcohol to a silica.

[0121] Ink jet record form created in the example 2 example 1 - It is an ink jet record form like an example 1 except having changed polyvinyl alcohol into 89% of thing average degree of polymerization 700 and whenever [ saponification ] in 1-9. - 11-19 were created.

[0122] The ink jet record form was evaluated like the example 1, and the result shown in a table 2 was obtained.

[0123]

[A table 2]

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-11 (比較例)	48%	10 ml/m <sup>2</sup>	×	△
記録用紙-12 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-13 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-14 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-15 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-16 (本発明)	54%	14 ml/m <sup>2</sup>	△	◎
記録用紙-17 (本発明)	51%	19 ml/m <sup>2</sup>	◎	◎
記録用紙-18 (本発明)	45%	22 ml/m <sup>2</sup>	○	○
記録用紙-19 (本発明)	40%	25 ml/m <sup>2</sup>	○	○

[0124] When the low thing of the average degree of polymerization of polyvinyl alcohol is used from the result shown in a table 2, in not using a hardening agent, it turns out that film formation nature deteriorates also in an ink jet record form (- 1 two) with the comparatively high amount of polyvinyl alcohol, film formation nature is improved by the activity of a hardening agent, and the same effectiveness as an example 1 is acquired although the assessment as an ink jet record form is almost impossible.

[0125] It is an ink jet record form like an example 1 except having changed polyvinyl alcohol into 88% of thing average degree of polymerization 3500 and whenever [ saponification ] in example 3 example 1. - 21-29 were created. The effectiveness same with having been obtained in the place evaluated like the example 1 and the example 1 was checked.

[0126] It sets in the example 4 example 1, and is an ink jet record form. - It is an ink jet record form like an example 1 except having changed the hardening agent into ethylene glycol diglycidyl ether in 6-9 (an addition being the same as that of an example 1). - 36-39 were created and it evaluated like the example 1. A result is shown in a table 3.

[0127]

[A table 3]

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-36 (本発明)	60%	13 ml/m <sup>2</sup>	○	○
記録用紙-37 (本発明)	58%	17 ml/m <sup>2</sup>	○	○
記録用紙-38 (本発明)	52%	21 ml/m <sup>2</sup>	◎	○
記録用紙-39 (本発明)	47%	23 ml/m <sup>2</sup>	◎	○

[0128] The result of a table 3 shows having high film formation nature and ink absorptivity compared with hardening agent un-adding, although film formation nature is a little low compared with a way acid when a hardening agent is changed into an epoxy system compound.

[0129] Ink jet record form created in the example 5 example 1 - Ink jet record form added in 1-9 so that a glycerol might be changed in an opening layer at 0.5 g/m<sup>2</sup> - 41-49 were created and it evaluated like the example 1. The obtained result is shown in a table 4.

[0130]

[A table 4]

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-4 1 (比較例)	7 4 %	11 ml/m <sup>2</sup>	△	○
記録用紙-4 2 (比較例)	4 6 %	14 ml/m <sup>2</sup>	△	△
記録用紙-4 3 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-4 4 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-4 5 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-4 6 (本発明)	7 2 %	14 ml/m <sup>2</sup>	○	◎
記録用紙-4 7 (本発明)	7 0 %	17 ml/m <sup>2</sup>	◎	◎
記録用紙-4 8 (本発明)	6 8 %	21 ml/m <sup>2</sup>	◎	◎
記録用紙-4 9 (本発明)	6 3 %	25 ml/m <sup>2</sup>	◎	◎

[0131] Ink jet record form of the result shown in a table 4 to this invention - As for 46-49, it turns out that film formation nature and glossiness are further improved by addition of a glycerol.

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[Translation done.]

**\* NOTICES \***

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- 3.In the drawings, any words are not translated.

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**CORRECTION OR AMENDMENT**

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[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law  
[Category partition] The 4th partition of the 2nd category  
[Publication date] February 6, Heisei 13 (2001. 2.6)

[Publication No.] JP,10-119423,A  
[Date of Publication] May 12, Heisei 10 (1998. 5.12)  
[Annual volume number] Open patent official report 10-1195  
[Application number] Japanese Patent Application No. 8-283635  
[The 7th edition of International Patent Classification]

B41M 5/00  
B32B 27/00  
D21H 27/00

[FI]

B41M	5/00	B
B32B	27/00	Z
D21H	5/00	Z

[Procedure amendment]  
[Filing Date] March 3, Heisei 12 (2000. 3.3)  
[Procedure amendment 1]  
[Document to be Amended] Description  
[Item(s) to be Amended] Claim 1  
[Method of Amendment] Modification  
[Proposed Amendment]

[Claim 1] The ink jet record form which is the opening layer in which at least one layer of this opening layer was formed of the flocculation of a hydrophilic binder and a non-subtlety particle on the base material in the ink jet record form which has at least one-layer opening layer, and is characterized by constructing the bridge over this hydrophilic binder with the hardening agent.

[Procedure amendment 2]  
[Document to be Amended] Description  
[Item(s) to be Amended] 0019  
[Method of Amendment] Modification  
[Proposed Amendment]

[0019] 1. Ink jet record form which is opening layer in which at least one layer of this opening layer was formed of flocculation of hydrophilic binder and non-subtlety particle on base material in ink jet record form which has at least one-layer opening layer, and is characterized by constructing bridge over this hydrophilic binder with hardening agent.

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[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11) 特許出願公開番号

特開平10-119423

(43) 公開日 平成10年(1998) 5月12日

(51) Int.Cl.<sup>8</sup>

識別記号

F I

B 4 1 M 5/00

B 4 1 M 5/00

B

B 3 2 B 27/00

B 3 2 B 27/00

Z

D 2 1 H 27/00

D 2 1 H 5/00

Z

審査請求 未請求 請求項の数 6 O L (全 10 頁)

(21) 出願番号

特願平8-283635

(22) 出願日

平成 8 年(1996)10月25日

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(54) 【発明の名称】 インクジェット記録用紙

(57) 【要約】

【課題】 必要最小限度の固体微粒子と親水性バインダーの使用により、高いインク吸収性の空隙構造を有するインクジェット記録用紙の提供。

【解決手段】 支持体上に、少なくとも1層の空隙層を有するインクジェット記録用紙において、該空隙層が親水性バインダーと無機微粒子の軟凝集により形成された空隙層を有し、該親水性バインダーが硬膜剤により架橋されていることを特徴とするインクジェット記録用紙。

## 【特許請求の範囲】

【請求項1】 支持体上に、少なくとも1層の空隙層を有するインクジェット記録用紙において、該空隙層が親水性バインダーと無機微粒子の軟凝集により形成された空隙層を有し、該親水性バインダーが硬膜剤により架橋されていることを特徴とするインクジェット記録用紙。

【請求項2】 前記親水性バインダーがポリビニルアルコールおよび／またはカチオン変成ポリビニルアルコールから選ばれる少なくとも1種の化合物であることを特徴とする請求項1に記載のインクジェット記録用紙。

【請求項3】 前記ポリビニルアルコールおよび／またはカチオン変成ポリビニルアルコールから選ばれる少なくとも1種の化合物の平均重合度が1000以上であることを特徴とする請求項2に記載のインクジェット記録用紙。

【請求項4】 前記空隙層が含有する無機微粒子が平均粒径が5～50nmのシリカであることを特徴とする請求項1、2又は3に記載のインクジェット記録用紙。

【請求項5】 前記硬膜剤が、ほう酸またはその塩および／又はポリエポキシ系化合物から選ばれる少なくとも1種の硬膜剤であることを特徴とする請求項1～4の何れか1項に記載のインクジェット記録用紙。

【請求項6】 前記空隙層が、分子中に少なくとも2個の水酸基を有しかつ分子量が300以下のポリオール類を含有することを特徴とする請求項1～5の何れか1項に記載のインクジェット記録用紙。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、水性インクを用いて記録を行うインクジェット記録用紙に関し、特にインク吸収層が高いインク吸収性を有する空隙層からなるインクジェット記録用紙において、皮膜の脆弱性を改善して高空隙容量を達成したインクジェット記録用紙に関するものである。

## 【0002】

【従来の技術】インクジェット記録は、インクの微小液滴を種々の作動原理により飛翔させて紙などの記録シートに付着させ、画像・文字などの記録を行うものであるが、比較的高速、低騒音、多色化が容易である等の利点を有している。この方式で従来から問題となっていたノズルの目詰まりとメンテナンスについては、インクおよび装置の両面から改良が進み、現在では各種プリンター、ファクシミリ、コンピューター端末等、さまざまな分野に急速に普及している。

【0003】このインクジェット記録方式で使用するインクジェット記録用紙としては、印字ドットの濃度が高く、色調が明るく鮮やかであること、インクの吸収が早く印字ドットが重なった場合に於いてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が必要以上に大きくなく、かつ周辺が滑らかでぼや

けないこと等が要求される。

【0004】特にインク吸収速度が遅い場合には、2色以上のインク液滴が重なって記録される際に、インクジェット記録用紙上で液滴がハジキ現象を起こしてムラになったり、また、異なる色の境界領域でお互いの色が滲んだりして画質を大きく低下させやすいために、インクジェット記録用紙としては高いインク吸収性を持たせるようにすることが必要である。

【0005】これらの問題を解決するために、従来から非常に多くの技術が提案されている。

【0006】例えば、特開昭52-53012号に記載されている低サイズ原紙に表面加工用の塗料を湿潤させたインクジェット記録用紙、特開昭55-5830号に記載されている支持体表面にインク吸収性の塗層を設けたインクジェット記録用紙、特開昭56-157号に記載されている被覆層中の顔料として非膠質シリカ粉末を含有するインクジェット記録用紙、特開昭57-107878号に記載されている無機顔料と有機顔料を併用したインクジェット記録用紙、特開昭58-110287号に記載されている2つの空孔分布ピークを有するインクジェット記録用紙、特開昭62-111782号に記載されている上下2層の多孔質層からなるインクジェット記録用紙、特開昭59-68292号、同59-123696号および同60-18383号などに記載されている不定形亀裂を有するインクジェット記録用紙、特開昭61-135786号、同61-148092号および同62-149475号等に記載されている微粉末層を有するインクジェット記録用紙、特開昭63-252779号、特開平1-108083号、同2-136279号、同3-65376号および同3-27976号等に記載されている特定の物性値を有する顔料や微粒子シリカを含有するインクジェット記録用紙、特開昭57-14091号、同60-219083号、同60-210984号、同61-20797号、同61-188183号、特開平5-278324号、同6-92011号、同6-183134号、同7-137431号、同7-276789号等に記載されているコロイド状シリカ等の微粒子シリカを含有するインクジェット記録用紙、および特開平2-276671号、同3-67684号、同3-215082号、同3-251488号、同4-67986号、同4-263983号および同5-16517号などに記載されているアルミナ水和物微粒子を含有するインクジェット記録用紙等が多数知られている。

【0007】上記した各種の方法は、一般に皮膜中に空隙を形成してそこにインクを吸収させるものであり、皮膜はインク吸収時には殆ど膨潤しない。このため、空隙形成による皮膜がインクを受容する際には、空隙量は皮膜の膜厚以下に原理的に制限されてしまう。

【0008】例えば、乾燥膜厚が40μmである皮膜に

において、固形分が均一な容積として仮に $22\mu\text{m}$ である皮膜を想定すると空隙量はインクジェット記録用紙 $1\text{m}^2$ 当たり $(40-22)=18\text{ml}/\text{m}^2$ しか有さないことになり、記録方式にもよるが最大インク量付近でインク吸収容量が不足し兼ねない場合が生じる。

【0009】インク吸収容量が不足するとインク液は記録紙表面に溢れて鮮明な画像を得ることができなくなる。

【0010】空隙構造を有する皮膜において、高い空隙容量を達成するためには塗布膜厚を増大させるのが最も効果的ではあるが、この場合には製造上コストが増大したりする不利があるだけでなく、固形分も一緒に増加するために皮膜のカールや脆弱性（特に低温下のヒビワレや支持体に対する膜接着性）が大きく低下しやすい。

【0011】このために、最小量のバインダー等の固形分を使用して出来るだけ多くの空隙を形成して全体の乾燥膜厚は極力低減することが好ましい。

【0012】バインダー等の固形分に対する空隙容量を高める端的な方法は、親水性バインダーに対する無機微粒子の割合を増加させることであり、他に不要な固形分を可能な限り使用しないことであるが、この場合には皮膜の脆弱性が極端に劣化してしまう問題点がある。

【0013】皮膜の脆弱性が劣化すると、インクジェット記録用紙の取り扱い時やインクジェットプリンターでの給紙や搬送時に皮膜剥がれが生じたり、あるいはヒビワレが生じて、このヒビワレに沿って画像が滲むという重大な欠点を生じる。

【0014】一方、皮膜中に空隙を設けることなくインク吸収層のバインダーの膨潤作用でインクを吸収、保持するタイプのインクジェット記録用紙も数多く知られている。

【0015】例えば、バインダーとしてゼラチン、カゼイン、澱粉、アルギン酸、ポリビニルアルコール、各種の変成ポリビニルアルコール、ポリビニルピロリドン、ポリエチレンオキサイド、ポリプロピレンオキサイド、カルボキシメチルセルロース、ヒドロキエチルセルロース、デキストラン、プルラン等の親水性バインダーを支持体上に塗布した記録紙やフィルム等も従来から数多く知られている。

【0016】これらのインクジェット記録用紙は高い光沢性や光学濃度を持った鮮明な画像が得られ、また、皮膜のバインダーのインク液に対する膨潤作用でインク液を受容するために高いインク吸収容量を本質的に保有することが出来る利点があるものの、インク吸収速度は空隙構造を有するインクジェット記録用紙に比べて劣り、特に高インク量の印字がされた部分でインク液滴同士のはじきによるざらつきが起りやすい欠点がある。

【0017】

【発明が解決しようとする課題】本発明は上記の実態に鑑みてなされたものであって、本発明が解決しようとする

る課題は、必要最小限度の固体微粒子と親水性バインダーの使用により、高いインク吸収性の空隙構造を有するインクジェット記録用紙を提供することにある。

【0018】

【課題を解決するための手段】本発明の上記目的は以下の構成により達成される。

【0019】1. 支持体上に、少なくとも1層の空隙層を有するインクジェット記録用紙において、該空隙層が親水性バインダーと無機微粒子の軟凝集により形成された空隙層を有し、該親水性バインダーが硬膜剤により架橋されていることを特徴とするインクジェット記録用紙。

【0020】2. 前記親水性バインダーがポリビニルアルコールおよび／またはカチオン変成ポリビニルアルコールから選ばれる少なくとも1種の化合物であることを特徴とする前記1に記載のインクジェット記録用紙。

【0021】3. 前記ポリビニルアルコールおよび／またはカチオン変成ポリビニルアルコールから選ばれる少なくとも1種の化合物の平均重合度が1000以上であることを特徴とする前記2に記載のインクジェット記録用紙。

【0022】4. 前記空隙層が含有する無機微粒子が平均粒径が $5\sim 50\text{nm}$ のシリカであることを特徴とする前記1、2又は3に記載のインクジェット記録用紙。

【0023】5. 前記硬膜剤が、ほう酸またはその塩および／またはポリエポキシ系化合物から選ばれる少なくとも1種の硬膜剤であることを特徴とする前記1～4の何れか1項に記載のインクジェット記録用紙。

【0024】6. 前記空隙層が、分子中に少なくとも2個の水酸基を有しかつ分子量が300以下のポリオール類を含有することを特徴とする前記1～5の何れか1項に記載のインクジェット記録用紙。

【0025】以下、本発明を詳細に説明する。

【0026】本発明のインクジェット記録用紙が有する空隙層は親水性のバインダーと無機微粒子の軟凝集により形成されるものである。

【0027】従来、皮膜中に空隙を形成する方法は種々知られており、例えば、①2種以上のポリマーを含有する均一な塗布液を支持体上に塗布し、乾燥過程でこれらのポリマーを互いに相分離させて空隙を形成する方法、②固体微粒子および親水性または疎水性バインダーを含有する塗布液を支持体上に塗布し、乾燥後に、インクジェット記録用紙を水或いは適当な有機溶媒を含有する液に浸漬して固体微粒子を溶解させて空隙を作成する方法、③皮膜形成時に発泡する性質を有する化合物を含有する塗布液を塗布後、乾燥過程でこの化合物を発泡させて皮膜中に空隙を形成する方法、④多孔質固体微粒子と親水性バインダーを含有する塗布液を支持体上に塗布し、多孔質微粒子中や微粒子間に空隙を形成する方法、⑤親水性バインダーに対して概ね等量以上（好ましくは1.0

倍以上)の容積を有する固体微粒子及びまたは微粒子油滴と親水性バインダーを含有する塗布液を支持体上に塗布して固体微粒子の間に空隙を作成する方法及び本発明に用いられる⑥平均粒径が約0.1  $\mu\text{m}$ 程度以下の無機固体微粒子を塗布液調製時または皮膜形成時に軟凝集させて2次粒子または3次元構造を形成して空隙を作成する方法等が知られている。

【0028】本発明のインクジェット記録用紙においては、高い光沢性、乾燥膜厚に対する高い空隙率および、空隙構造の保存中の安定性等の観点から、上記した中でも、⑥の軟凝集を形成する方法による空隙形成方法が用いられる。

【0029】本発明で用いられる軟凝集を形成して空隙構造を皮膜中に形成する方法は、好ましくは親水性バインダーを含有する水溶液中に分散状態にある1次超微粒子が、接触点が比較的制限された状態でお互いに凝集し合う状態を経由して形成される。

【0030】このような軟凝集構造は直線的もしくは分岐状に凝集体を形成したものが水溶液中に分散された状態や、あるいはこれらの凝集体が更に凝集し合って水溶液中で3次元網目構造をとる状態が含まれる。

【0031】いずれの場合であっても、この水溶液を支持体上に塗布乾燥することによって、形成された皮膜中に微細な空隙構造を形成することが出来る。

【0032】この様にして得られた皮膜中の微細な空隙の大きさは、概ね1次粒子の大きさからそれらの数倍程度の大きさであり、微細な大きさの空隙である特徴がある。

【0033】この様な軟凝集構造を形成する方法としては、例えば1次粒子がお互いに凝集しにくく、安定に存在できるような親水性バインダーを含有する水溶液中に、粒子の凝集を加速するような親水性ポリマーを極微量添加して僅かに凝集を形成する方法、あるいは1次粒子表面と弱い結合が出来るような水溶性バインダーを有する水溶液中で形成される。

【0034】本発明では、特に、後者の方法が空隙の量を比較的コントロールしやすく安定に形成しやすいこと、使用する微粒子の量に比較してより多い空隙量が得られること、さらには皮膜の光沢性がより高い皮膜が得られることから好ましい。

【0035】後者の方法により空隙を形成する場合、1次粒子の粒径としては概ね0.003~0.05  $\mu\text{m}$ の1次粒子を用いることがより高い光沢性が得られることから好ましい。特に好ましい1次粒子は0.004  $\mu\text{m}$ ~0.02  $\mu\text{m}$ のものである。

【0036】本発明の無機微粒子としては、例えば、シリカ、珪酸マグネシウムや珪酸カルシウム等の珪酸塩、水酸化アルミニウム、水酸化亜鉛、合成ヘクトライト等各種スメクタイト粘土(例えば特開平7-81210号および同6-184998号などに記載された粘土)等

が挙げられる。

【0037】また、本発明の親水性バインダーとしては、従来公知の各種親水性バインダーが用いられ、例えばゼラチンまたはゼラチン誘導体、ポリビニルピロリドン(平均分子量が約20万以上が好ましい)、プルラン、ポリビニルアルコールまたはその誘導体(平均分子量が約20万以上が好ましい)、ポリエチレングリコール(平均分子量が10万以上が好ましい)、カルボキシメチルセルロース、ヒドロキシエチルセルロース、デキストラン、デキストリン、ポリアクリル酸およびその塩、寒天、 $\kappa$ -カラギーナン、 $\lambda$ -カラギーナン、 $\iota$ -カラギーナン、キサンテンガム、ローカストビーンガム、アルギン酸、アラビアゴム、プルラン、特開平7-195826号および同7-97577号に記載のポリアルキレンオキサイド系共重合性ポリマー、水溶性ポリビニルブチラール、あるいは、特開昭62-245260号に記載のカルボキシル基やスルホン酸基を有するビニルモノマーの単独またはこれらのビニルモノマーを繰り返して有する共重合体等のポリマーを挙げることができる。これらの親水性バインダーは単独で使用しても良く、2種以上を併用しても良い。

【0038】特に好ましい親水性バインダーは、ポリビニルアルコールまたはカチオン変性ポリビニルアルコールである。

【0039】本発明で好ましく用いられるポリビニルアルコールは平均重合度が300~4000のものが好ましく用いられ、特に平均分子量が1000以上のものが得られる皮膜の脆弱性が良好であることから好ましい。また、ポリビニルアルコールのケン化度は70~100%のものが好ましく、80~100%のものが特に好ましい。また、カチオン変性ポリビニルアルコールは、カチオン性基を有するエチレン性不飽和単量体と酢酸ビニルとの共重合体をケン化することにより得られる。

【0040】カチオン性基を有するエチレン性不飽和単量体としては、例えばトリメチルー(2-アクリルアミド-2, 2-ジメチルエチル)アンモニウムクロライド、トリメチルー(3-アクリルアミド-3, 3-ジメチルプロピル)アンモニウムクロライド、N-ビニルイミダゾール、N-ビニルー2-メチルイミダゾール、N-(3-ジメチルアミノプロピル)メタクリルアミド、ヒドロキシエチルトリメチルアンモニウムクロライド、トリメチルー(メタクリルアミドプロピル)アンモニウムクロライド、N-(1, 1-ジメチルー3-ジメチルアミノプロピル)アクリルアミド等が挙げられる。

【0041】カチオン変性ポリビニルアルコールのカチオン変性基含有単量体の比率は、酢酸ビニルに対して0.1~10モル%、好ましくは0.2~5モル%である。

【0042】カチオン変性ポリビニルアルコールの重合

度は通常500~4000、好ましくは1000~4000が好ましい。

【0043】また、カチオン変成ポリビニルアルコールのケン化度は通常60~100モル%、好ましくは70~99モル%である。

【0044】本発明で特に好ましいのは微粒子シリカを1次粒子として使用し、親水性バインダーとしてポリビニルアルコールまたは変性ポリビニルアルコールを用いる場合である。この場合、微粒子シリカ表面のシラノール基とビニルアルコールの水酸基が弱い水素結合を行い、軟凝集体が形成される。

【0045】1次粒子シリカとしては平均粒径が特に0.02 $\mu$ m以下のものが好ましく、特に0.015~0.006 $\mu$ mのものが最も好ましい。また、これらが連結した2次粒子としては0.02~0.2 $\mu$ m、好ましくは0.03~0.1 $\mu$ m程度になるようにするのが好ましい。

【0046】この様な微粒子シリカは通常、気相法と呼ばれる合成方法で合成された微粒子シリカが好ましく用いられる。

【0047】本発明において、軟凝集構造を形成するのに特に好ましい親水性バインダーはポリビニルアルコールである。

【0048】前記親水性バインダーと前記無機固体微粒子の比率は、重量比で概ね1:15~1:1であり、好ましくは1:10~1:2の範囲である。

【0049】ポリビニルアルコールと微粒子シリカを用いて軟凝集体を含む皮膜を形成する場合についてその方法の例について以下に説明する。

【0050】pHを6~8、温度約40℃に保ったポリビニルアルコール水溶液（概ね3~15%）中に、シリカ微粒子分散液（概ね5~15%）を強撹拌しながら徐々に添加し、添加終了後に超音波分散機や高速ホモジナイザーなどにより分散する。この場合必要に応じて各種の界面活性剤やメタノール、アセトン、酢酸エチルなどの水混和性の有機溶媒を使用するのは均一な塗布液を調製する上で好都合である。

【0051】ついで、各種の添加剤を添加後、塗布に必要な粘度に調整して支持体上に公知の方法で塗布し乾燥することで上記空隙を有する皮膜が得られる。

【0052】本発明のインクジェット記録用紙は、高い空隙率を皮膜の脆弱性を劣化させずに得るために、前記親水性バインダーが硬膜剤により硬膜されていることが必要である。

【0053】硬膜剤は、一般的には前記親水性バインダーと反応し得る基を有する化合物あるいは親水性バインダーが有する異なる基同士の反応を促進するような化合物であり、親水性バインダーの種類に応じて適宜選択して用いられる。

【0054】硬膜剤の具体例としては、例えば、エポキ

シ系硬膜剤（ジグリシジルエチルエーテル、エチレングリコールジグリシジルエーテル、1,4-ブタンジオールジグリシジルエーテル、1,6-ジグリシジルシクロヘキサン、N,N-ジグリシジル-4-グリシジルオキシアニリン、ソルビトールポリグリシジルエーテル、グリセロールポリグリシジルエーテル等）、アルデヒド系硬膜剤（ホルムアルデヒド、グリオキサール等）、活性ハロゲン系硬膜剤（2,4-ジクロロ-4-ヒドロキシ-1,3,5-スートリアジン等）、活性ビニル系化合物（1,3,5-トリシアクリロイル-ヘキサヒドロ-スートリアジン、ビスビニルスルホンメチルエーテル等）、ほう酸およびその塩、ほう砂、アルミ明礬等が挙げられる。

【0055】特に好ましい親水性バインダーとしてポリビニルアルコールおよび/またはカチオン変成ポリビニルアルコールから選ばれる少なくとも1種の化合物を使用する場合には、ほう酸およびその塩および/またはエポキシ系硬膜剤から選ばれる少なくとも1種の硬膜剤を使用するのが好ましい。

【0056】最も好ましいのはほう酸およびその塩から選ばれる硬膜剤である。

【0057】本発明で、ほう酸またはその塩としては、硼素原子を中心原子とする酸素酸およびその塩のことを示し、具体的にはオルトほう酸、二ほう酸、メタほう酸、四ほう酸、五ほう酸、および八ほう酸およびそれらの塩が含まれる。

【0058】上記硬膜剤の使用量は親水性バインダーの種類、硬膜剤の種類、無機微粒子の種類や親水性バインダーに対する比率等により変化するが、概ね親水性バインダ1g当たり1~200mg、好ましくは5~100mgである。

【0059】上記硬膜剤は、空隙層を構成する塗布液を塗布する際に空隙層形成の塗布液中及びまたは空隙層に隣接するその他の層を形成する塗布液中に添加してもよく、あるいは予め硬膜剤を含有する塗布液を塗布してある支持体上に、前記空隙層を形成する塗布液を塗布したり、さらには空隙層を形成する硬膜剤非含有の塗布液を塗布乾燥後に硬膜剤溶液をオーバーコートするなどして空隙層に硬膜剤を供給することができるが、好ましくは製造上の効率及び空隙層の形成時のヒビわれ防止の観点から、空隙層を形成する塗布液またはこれに隣接する層の塗布液中に硬膜剤を添加して、空隙層を形成すると同時に硬膜剤を供給するのが好ましい。

【0060】空隙層を形成するのが超微粒子シリカおよびポリビニルアルコールである特に好ましい態様においては、空隙層を形成する塗布液中に予め硬膜剤を添加しておき、一定時間（好ましくは10分以上、特に好ましくは30分以上）経過してから支持体上に塗布・乾燥するとより高い空隙率を皮膜の脆弱性を悪化させることなく達成することが出来る。

【0061】本発明のインクジェット記録用紙は空隙層が更に分子中に少なくとも2個の水酸基を有し、かつ分子量が300以下のポリオール類を含有する場合、皮膜の脆弱性がさらに改善された空隙層を得ることが出来る。

【0062】その様なポリオール類としては例えば、エチレングリコール、ジエチレングリコール、平均分子量が300以下のポリエチレングリコール、グリセリン、ブタンジオール、ブタントリオール、およびトリエタノールアミン等を挙げることが出来る。

【0063】上記ポリオール類の使用量は親水性バインダー1g当たり0.01~2gが好ましく、より好ましくは0.05~1gの範囲である。

【0064】本発明のインクジェット記録用紙は最大インク量がインクジェット記録用紙1m<sup>2</sup>当たり20ml/m<sup>2</sup>以上であるようなインクジェット記録方法において特に本発明の効果が著しい。

【0065】本発明のインクジェット記録用紙の空隙容量は印字される最大インク容量の90%以上、特に95%以上有することが好ましい。また、空隙層を構成するインク受容層の乾燥膜厚は概ね50μm以下にすることがひび割れ等の皮膜の物理的特性を悪化させないために好ましい。

【0066】一方、空隙容量の空隙層全体の容量に対する比率は概ね70容量%以下にするのが皮膜の物理的強度や脆弱性の観点から好ましい。

【0067】本発明のインクジェット記録用紙は上記条件を満足する空隙容量として20~30ml/m<sup>2</sup>の範囲の量が適当である。

【0068】本発明の空隙層および必要に応じて設けられるその他の層には、前記した以外に各種の添加剤を添加することが出来る。

【0069】例えば、ポリスチレン、ポリアクリル酸エステル類、ポリメタクリル酸エステル類、ポリアクリルアミド類、ポリエチレン、ポリプロピレン、ポリ塩化ビニル、ポリ塩化ビニリデン、またはこれらの共重合体、尿素樹脂、またはメラミン樹脂等の有機ラテックス微粒子、流動パラフィン、ジオクチルフタレート、トリクレジルホスフェート、シリコンオイル等の油滴微粒子、アニオン、カチオン、ノニオン等の各種界面活性剤、特開昭57-74193号、同57-87988号及び同62-261476号に記載の紫外線吸収剤、特開昭57-74192号、同57-87989号、同60-72785号、同61-146591号、特開平1-95091号及び同3-13376号等に記載されている退色防止剤、特開昭59-42993号、同59-52689号、同62-280069号、同61-242871号および特開平4-219266号等に記載されている蛍光増白剤、硫酸、リン酸、クエン酸、水酸化ナトリウム、水酸化カリウム、炭酸カリウム等のpH調整剤、消

泡剤、防腐剤、増粘剤、帯電防止剤、マツト剤等の公知の各種添加剤を含有させることもできる。

【0070】本発明のインク記録面側の任意の構成層中には、画像の耐水化剤として特開昭56-84992号のポリカチオン高分子電解質、特開昭57-36692号の塩基性ラテックスポリマー、特公平4-15744号、特開昭61-58788号、同62-174184号等記載のポリアリルアミン、特開昭61-47290号記載のアルカリ金属弱酸塩等を一種以上用いることができる。

【0071】上記、空隙層は2層以上から構成されていてもよく、この場合、それらの空隙層の構成は前述した範囲内で有れば異なっても良い。

【0072】本発明でインクジェット記録用紙の支持体としては、従来インクジェット用記録用紙として公知のものを適宜使用できるが、より高い濃度で鮮明な画像を得るためには支持体中にインク液が浸透しない疎水性支持体を用いるのが好ましい。

【0073】透明支持体としては、例えば、ポリエステル系樹脂、ジアセテート系樹脂、トリアセテート系樹脂、アクリル系樹脂、ポリカーボネート系樹脂、ポリ塩化ビニル系樹脂、ポリイミド系樹脂、セロハン、セルロイド等の材料からなるフィルム等が挙げられ、中でもOHPとして使用されたときの輻射熱に耐える性質のものが好ましく、ポリエチレンテレフタレートが特に好ましい。このような透明な支持体の厚さとしては、約10~200μmが好ましい。透明支持体のインク受容層側およびバック層側には公知の下引き層を設けることが、インク受容層やバック層と支持体の接着性の観点から好ましい。

【0074】また、透明である必要のない場合に用いる支持体としては、例えば、基紙の少なくとも一方に白色顔料等を添加したポリオレフィン樹脂被覆層を有する樹脂被覆紙（いわゆるRCペーパー）、ポリエチレンテレフタレートに白色顔料を添加してなるいわゆるホワイトペットが好ましい。

【0075】上記支持体とインク受像層の接着強度を大きくする等の目的で、インク受容層の塗布に先立って、支持体にコロナ放電処理や下引処理等を行うことが好ましい。さらに、本発明の記録シートは必ずしも無色である必要はなく、着色された記録シートであってもよい。

【0076】本発明のインクジェット記録用紙では原紙支持体の両面をポリエチレンでラミネートした紙支持体を用いることが、記録画像が写真画質に近く、しかも低コストで高品質の画像が得られるために特に好ましい。そのようなポリエチレンでラミネートした紙支持体について以下に説明する。

【0077】紙支持体に用いられる原紙は木材パルプを主原料とし、必要に応じて木材パルプに加えてポリプロピレンなどの合成パルプあるいはナイロンやポリエス

ルなどの合成繊維を用いて抄紙される。木材パルプとしてはLBKP、LBSP、NBKP、NBSP、LDP、NDP、LUKP、NUKPのいずれも用いることが出来るが短繊維分の多いLBKP、NBSP、LBSP、NDP、LDPをより多く用いることが好ましい。但し、LBSPおよびまたはLDPの比率は10重量%以上、70重量%以下が好ましい。

【0078】上記パルプは不純物の少ない化学パルプ（硫酸塩パルプや亜硫酸塩パルプ）が好ましく用いられ、又、漂白処理を行って白色度を向上させたパルプも有用である。

【0079】原紙中には、高級脂肪酸、アルキルケテンダイマー等のサイズ剤、炭酸カルシウム、タルク、酸化チタンなどの白色顔料、スターチ、ポリアクリルアミド、ポリビニルアルコール等の紙力増強剤、蛍光増白剤、ポリエチレングリコール類等の水分保持剤、分散剤、4級アンモニウム等の柔軟化剤などを適宜添加することが出来る。

【0080】抄紙に使用するパルプの濾水度はCSFの規定で200～500ccが好ましく、また、叩解後の繊維長がJIS-P-8207に規定される24メッシュ残分重量%と42メッシュ算分の重量%との和が30乃至70%が好ましい。なお、4メッシュ残分の重量%は20重量%以下であることが好ましい。

【0081】原紙の坪量は30乃至250gが好ましく、特に50乃至200gが好ましい。原紙の厚さは40乃至250μmが好ましい。

【0082】原紙は抄紙段階または抄紙後にカレンダー処理して高平滑性を与えることも出来る。原紙密度は0.7乃至1.2g/m<sup>2</sup>（JIS-P-8118）が一般的である。更に原紙剛度はJIS-P-8143に規定される条件で20乃至200gが好ましい。

【0083】原紙表面には表面サイズ剤を塗布しても良く、表面サイズ剤としては前記原紙中添加できるサイズと同様のサイズ剤を使用できる。

【0084】原紙のpHはJIS-P-8113で規定された熱水抽出法により測定された場合、5～9であることが好ましい

原紙表面および裏面を被覆するポリエチレンは、主として低密度のポリエチレン（LDPE）および／または高密度のポリエチレン（HDPE）であるが他のLLDPEやポリプロピレン等も一部使用することが出来る。

【0085】特にインク受容層側のポリエチレン層は写真用印画紙で広く行われているようにルチルまたはアナターゼ型の酸化チタンをポリエチレン中に添加し、不透明度および白色度を改良したものが好ましい。酸化チタン含有量はポリエチレンに対して概ね3～20重量%、好ましくは4～13重量%である。

【0086】ポリエチレン被覆紙は光沢紙として用いることも、また、ポリエチレンを原紙表面上に溶融押し出

してコーティングする際にいわゆる型付け処理を行って通常の写真印画紙で得られるようなマット面や絹目面を形成した物も本発明で使用できる。

【0087】原紙の表裏のポリエチレンの使用量はインク受容層やバック層を設けた後で低湿および高湿化でのカールを最適化するように選択されるが、概ねインク受容層側のポリエチレン層が20～40μm、バック層側が10～30μmの範囲である。

【0088】更に上記ポリエチレン被覆紙支持体は以下の特性を有していることが好ましい。

【0089】①引張り強さ：JIS-P-8113で規定される強度で縦方向が2乃至30kg、横方向が1乃至20kgであることが好ましい

②引き裂き強度：JIS-P-8116による規定方法で縦方向が10乃至200g、横方向が20乃至200gが好ましい

③圧縮弾性率 $\geq 10^3 \text{ kgf/cm}^2$

④表面ベック平滑度：JIS-P-8119に規定される条件で20秒以上、特に好ましくは500秒以上が光沢面としては好ましいが、いわゆる型付け品ではこれ以下であっても良い

⑤不透明度：JIS-P-8138による方法で85%以上、特に90%以上が好ましい。

【0090】本発明のインクジェット記録用紙の空隙層および下引き層など必要に応じて適宜設けられる各種の親水性層を支持体上に塗布する方法は公知の方法から適宜選択して行うことが出来る。好ましい方法は、各層を構成する塗布液を支持体上に塗設して乾燥して得られる。この場合、2層以上を同時に塗布することもでき、特に全ての親水性バインダー層を1回の塗布で済ます同時塗布が好ましい。

【0091】塗布方式としては、ロールコーティング法、ロッドバーコーティング法、エアナイフコーティング法、スプレーコーティング法、カーテン塗布方法あるいは米国特許第2,681,294号記載のホッパーを使用するエクストルージョンコート法が好ましく用いられる。

【0092】本発明のインクジェット記録用紙を用いて画像記録する際には、水性インクを用いた記録方法が用いられる。

【0093】本発明で言う水性インクとは、下記着色剤及び液媒体、その他の添加剤から成る記録液体である。着色剤としてはインクジェットで公知の直接染料、酸性染料、塩基性染料、反応性染料あるいは食品用色素等の水溶性染料が使用できる。

【0094】水性インクの溶媒としては、水及び水溶性の各種有機溶剤、例えば、メチルアルコール、イソプロピルアルコール、n-ブチルアルコール、tert-ブチルアルコール、イソブチルアルコール等のアルコール類；ジメチルホルムアミド、ジメチルアセトアミド等の



アミド類；アセトン、ジアセトンアルコール等のケトンまたはケトンアルコール類；テトラヒドロフラン、ジオキサン等のエーテル類；ポリエチレングリコール、ポリプロピレングリコール等のポリアルキレングリコール類；エチレングリコール、プロピレングリコール、ブチレングリコール、トリエチレングリコール、1, 2, 6-ヘキサントリオール、チオジグリコール、ヘキシレングリコール、ジエチレングリコール、グリセリン、トリエタノールアミン等の多価アルコール類；エチレングリコールメチルエーテル、ジエチレングリコールメチル

(又はエチル)エーテル、トリエチレングリコールモノブチルエーテル等の多価アルコールの低級アルキルエーテル類等が挙げられる。

【0095】これらの多くの水溶性有機溶剤の中でも、ジエチレングリコール、トリエタノールアミンやグリセリン等の多価アルコール類、トリエチレングリコールモノブチルエーテルの多価アルコールの低級アルキルエーテル等は好ましいものである。

【0096】その他の水性インクの添加剤としては、例えばpH調節剤、金属封鎖剤、防カビ剤、粘度調整剤、表面張力調整剤、湿潤剤、界面活性剤、及び防錆剤等が挙げられる。

【0097】水性インク液はインクジェット記録用紙に対する濡れ性を良好にするために、20℃において、25～50dyn/cm、好ましくは30～40dyn/cmの範囲内の表面張力を有するのが好ましい。

【0098】

【実施例】以下に本発明の実施例を挙げて説明するが、本発明はこれらの例に限定されるものではない。なお、実施例中で「%」は特に断りのない限り絶対重量%を示し、添加量は各々インクジェット記録用紙1m<sup>2</sup>当たりの量を示す。

【0099】実施例1

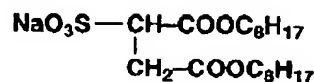
平均粒径が約0.07μmの表面がアニオン性の超微粒子シリカ粉末160gを純水1000ml中に添加し、高速ホモジナイザーで分散した。次にこのシリカ水分散液(I)中に、平均重合度が1700でケン化度が90%の5%ポリビニルアルコール水溶液(II)(界面活性剤-1を0.3重量%含有)1600mlを徐々に添加した。得られた液を高速ホモジナイザーにて分散して半透明状の塗布液を得た。

【0100】次に、上記のようにして得られた塗布液を、170g/m<sup>2</sup>の原紙両面をポリエチレンで被覆した紙支持体(厚さ240μm、記録面側のポリエチレン層中に9重量%のアナターゼ型二酸化チタン含有。)上の記録面側に、湿潤膜厚が150μmになるように塗布し、20～40℃の風で乾燥してインクジェット記録用紙-1(比較例)を得た。

【0101】

【化1】

## 界面活性剤-1



【0102】次に、インクジェット記録用紙-1において、以下のように変更した以外はインクジェット記録用紙-1と同様にしてインクジェット記録用紙-2～9を作成した。

【0103】〔インクジェット記録用紙-2〕ポリビニルアルコール水溶液(II)1600mlをポリビニルアルコール水溶液(II)800mlと界面活性剤-1の0.3重量%水溶液800mlの混合液に変更した以外はインクジェット記録用紙-1と同じ。

【0104】〔インクジェット記録用紙-3〕ポリビニルアルコール水溶液(II)1600mlをポリビニルアルコール水溶液(II)530mlと界面活性剤-1の0.3重量%水溶液1070mlの混合液に変更した以外はインクジェット記録用紙-1と同じ。

【0105】〔インクジェット記録用紙-4〕ポリビニルアルコール水溶液(II)1600mlをポリビニルアルコール水溶液(II)400mlと界面活性剤-1の0.3重量%水溶液1200mlの混合液に変更した以外はインクジェット記録用紙-1と同じ。

【0106】〔インクジェット記録用紙-5〕ポリビニルアルコール水溶液(II)1600mlをポリビニルアルコール水溶液(II)320mlと界面活性剤-1の0.3重量%水溶液1280mlの混合液に変更した以外はインクジェット記録用紙-1と同じ。

【0107】〔インクジェット記録用紙-6〕インクジェット記録用紙-2を作成するのに使用した塗布液に、硬膜剤として四ほう酸ナトリムの2重量%水溶液60mlを添加し、高速ホモジナイザーで30分間分散した後、インクジェット記録用紙-2と同様にして塗布して得られたインクジェット記録用紙。

【0108】〔インクジェット記録用紙-7〕インクジェット記録用紙-3を作成するのに使用した塗布液に、硬膜剤として四ほう酸ナトリムの2重量%水溶液を50ml添加し、高速ホモジナイザーで再度30分間分散した後、インクジェット記録用紙-3と同様にして塗布して得られたインクジェット記録用紙。

【0109】〔インクジェット記録用紙-8〕インクジェット記録用紙-4を作成するのに使用した塗布液に、硬膜剤として四ほう酸ナトリムの2重量%水溶液を60ml添加し、高速ホモジナイザーで再度30分間分散した後、インクジェット記録用紙-4と同様にして塗布して得られたインクジェット記録用紙。

【0110】〔インクジェット記録用紙-9〕インクジェット記録用紙-5を作成するのに使用した塗布液に、

硬膜剤として四ほう酸ナトリムの2重量%水溶液を70 ml 添加し、高速ホモジナイザーで再度30分間分散した後、インクジェット記録用紙-5と同様にして塗布して得られたインクジェット記録用紙。

【0111】得られた各々のインクジェット記録用紙について、以下の項目について評価した。

【0112】(1) 光沢度：日本電色工業株式会社製変角光沢度計(VGS-1001DP)を用いて60度光沢を測定した。

【0113】(2) 空隙量：インク吐出量を制御できるオンデマンド型インクジェットプリンターを用い、YとMのベタ領域に、白抜き(未印字)の細線パターンを印字し、インクが溢れることなく細線が明瞭に識別し得る最大インク量を空隙量として求めた。

【0114】(3) インク吸収性：セイコーエプソン(株)製インクジェットプリンター(MJ-5100C)でカラー画像の印字を行い、高インク領域における画質を評価した

◎：インク溢れによるシャドー部の画像のつぶれがなく、また、ヒビワレに伴うしみもない

○：インク溢れによるシャドー部の画像のつぶれがあるがヒビワレに伴うしみはない

△：シャドー部のつぶれがあり、またヒビワレに伴うしみがあるが画像としては概ね識別できる

×：画像のつぶれ、インクの溢れ、ヒビワレに伴うしみ、印字部の膜剥がれが甚大で画像としてほとんど識別不能。

【0115】(4) 造膜性：印字前に膜面の造膜性を以下の基準で判断した。

【0116】

◎：ヒビワレはなく、23℃、相対湿度80%で表面を指で強く擦っても膜が剥がれない

○：ヒビワレはなく、また指で強く擦れば僅かに膜が剥がれることがあるが、通常の扱いでは膜が剥がれることはない

△：全面に微小なひび割れ状態になっているが、インクジェットプリンターで搬送時に膜が剥がれることはない

×：インクジェットプリンターで搬送時に容易に巻くが剥がれ落ちたり、塗布乾燥後に自然に巻くが剥がれ落ちる。

【0117】得られた結果を表1に示す。

【0118】

【表1】

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-1(比較例)	7.2%	11 ml/m <sup>2</sup>	△	○
記録用紙-2(比較例)	4.2%	14 ml/m <sup>2</sup>	△	△
記録用紙-3(比較例)	測定不能	評価不能	評価不能	×
記録用紙-4(比較例)	測定不能	評価不能	評価不能	×
記録用紙-5(比較例)	測定不能	評価不能	評価不能	×
記録用紙-6(本発明)	6.6%	15 ml/m <sup>2</sup>	○	◎
記録用紙-7(本発明)	6.2%	18 ml/m <sup>2</sup>	◎	◎
記録用紙-8(本発明)	6.0%	22 ml/m <sup>2</sup>	◎	◎
記録用紙-9(本発明)	5.6%	26 ml/m <sup>2</sup>	◎	○

【0119】表1に示す結果から、硬膜剤を使用しないインクジェット記録用紙(1~5)においては、シリカ微粒子に対するポリビニルアルコールの量を減量した場合、皮膜としての造膜性が低下し、ポリビニルアルコールに対するシリカの比率が2~4(インクジェット記録用紙-1、2)においては比較的良好な造膜性が得られるものの空隙量が不十分でこの範囲ではインク吸収性が不足して良好な画像が得られない。

【0120】これに対して、本発明のインクジェット記録用紙-6~9は、優れた造膜性を有しており、シリカに対してポリビニルアルコールの量を減少させても良好

な造膜性を維持しつつ高い光沢性と良好なインク吸収性を有する事がわかる。

【0121】実施例2

実施例1で作成したインクジェット記録用紙-1~9において、ポリビニルアルコールを平均重合度700、ケン化度89%のものに変更した以外は実施例1と同様にしてインクジェット記録用紙-11~19を作成した。

【0122】実施例1と同様にしてインクジェット記録用紙を評価し、表2に示す結果を得た。

【0123】

【表2】

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-11 (比較例)	48%	10 ml/m <sup>2</sup>	×	△
記録用紙-12 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-13 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-14 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-15 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-16 (本発明)	54%	14 ml/m <sup>2</sup>	△	◎
記録用紙-17 (本発明)	51%	19 ml/m <sup>2</sup>	◎	◎
記録用紙-18 (本発明)	45%	22 ml/m <sup>2</sup>	○	○
記録用紙-19 (本発明)	40%	25 ml/m <sup>2</sup>	○	○

【0124】表2に示す結果から、ポリビニルアルコールの平均重合度の低いものを使用した場合、硬膜剤を使用しない場合には、ポリビニルアルコールの量が比較的高いインクジェット記録用紙（-1、2）においても造膜性が劣化しインクジェット記録用紙としての評価が殆ど不可能であるが、硬膜剤の使用で造膜性が改善され実施例1と同様の効果が得られることがわかる。

#### 【0125】実施例3

実施例1において、ポリビニルアルコールを平均重合度3500、ケン化度88%のものに変更した以外は実施例1と同様にしてインクジェット記録用紙-21～29

を作成した。実施例1と同様にして評価した所、実施例1で得られたのと同様の効果を確認した。

#### 【0126】実施例4

実施例1において、インクジェット記録用紙-6～9において、硬膜剤を、エチレングリコールジグリシジルエーテルに変更（添加量は実施例1と同一）した以外は実施例1と同様にしてインクジェット記録用紙-36～39を作成し実施例1と同様にして評価した。結果を表3に示す。

#### 【0127】

#### 【表3】

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-36 (本発明)	60%	13 ml/m <sup>2</sup>	○	○
記録用紙-37 (本発明)	58%	17 ml/m <sup>2</sup>	○	○
記録用紙-38 (本発明)	52%	21 ml/m <sup>2</sup>	◎	○
記録用紙-39 (本発明)	47%	23 ml/m <sup>2</sup>	◎	○

【0128】表3の結果から、硬膜剤をエポキシ系化合物に変更したところ、造膜性がほう酸に比べてやや低いものの硬膜剤未添加に比べて高い造膜性とインク吸収性を有していることがわかる。

#### 【0129】実施例5

実施例1で作成したインクジェット記録用紙-1～9に

において、空隙層中にグリセリンを0.5 g/m<sup>2</sup>に成るように添加したインクジェット記録用紙-41～49を作成し実施例1と同様にして評価した。得られた結果を表4に示す。

#### 【0130】

#### 【表4】

インクジェット記録用紙	光沢度	空隙量	インク吸収性	造膜性
記録用紙-41 (比較例)	74%	11 ml/m <sup>2</sup>	△	○
記録用紙-42 (比較例)	46%	14 ml/m <sup>2</sup>	△	△
記録用紙-43 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-44 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-45 (比較例)	測定不能	評価不能	評価不能	×
記録用紙-46 (本発明)	72%	14 ml/m <sup>2</sup>	○	◎
記録用紙-47 (本発明)	70%	17 ml/m <sup>2</sup>	◎	◎
記録用紙-48 (本発明)	68%	21 ml/m <sup>2</sup>	◎	◎
記録用紙-49 (本発明)	63%	25 ml/m <sup>2</sup>	◎	◎

【0131】表4に示す結果から、本発明のインクジェット記録用紙-46～49は、グリセリンの添加により造膜性と光沢性がいっそう改善されることがわかる。

#### 【0132】

【発明の効果】以上、本発明のインクジェット記録用紙

の構成を用いれば、必要最小限度の固体微粒子と親水性バインダーの使用により、高いインク吸収性の空隙構造を有し、しかも高い光沢性を有するインクジェット記録用紙を得る事ができる。